THE CHARACTERISATION OF CRUDE OILS AND THE ANALYSIS OF BY- PRODUCTS PRODUCED IN PETROCHEMICAL PLANTS.

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I hereby certify that the work described in this thesis is the result of my own investigations except where otherwise indicated.

Signed .....Candidate

Signed .....Director of studies

DECLARATION

I hereby declare that this work has not already been accepted for any degree and is not being concurrently submitted in canditature for any degree.

Signed .....Candidate

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SUMMARY.

The use of solid phase extraction (SPE) in conjunction with gas chromatography combined with mass spectrometry (GC/MS) has been evaluated for identifying aromatic compounds in crude oils. A standard hexane solution of polyaromatic hydrocarbons (PAHs) was used for SPE method development using a coupled silica, cyano cartridge system. Quantitative GC/MS analysis confirmed that the SPE method developed provided potential for the high recovery of the PAHs within a single solvent fraction. The SPE method proved unsuccessful for the isolation of aromatic compounds from crude oil since the oil itself modified the mobile phase.

Column chromatography with silica as stationary phase provided a means of fractionating crude oil such that the aromatic profile could be determined by GC/MS. With this approach in excess of forty aromatic compounds were found to be present within a sample of Libyan crude oil . The use of supercritical fluid extraction was also evaluated as a rapid means for the isolation of aromatic species from crude oil. The oil was loaded onto a silica support prior to extraction. Using high density supercritical fluid carbon dioxide only aliphatic hydrocarbons could be isolated from the crude oil sample.

Studies involving chromatographic and spectroscopic techniques were also performed to characterise by-products associated with petrochemical plant and gas field industrial operations. An impurity isolated from a urea plant was tentatively identified as a polyamide species whereas an impurity obtained from a methanol plant was found to be composed of a mixture of hydrocarbons ranging from C-12 to C-33. A deposit obtained from the Sahel gas field was determined to be largely composed of a complex mixture of inorganic compounds.

List of Abbreviations

AAS	Atomic Absorption Spectroscopy
MS	Mass Spectrometry
EI	Electron Ionization
CI	Chemical Ionization
LC	Liquid Chromatography
HPLC	High Performance Liquid Chromatography
GC	Gas Chromatography
GC/MS	Combined Gas Chromatography/Mass Spectrometry
LC/MS	Combined Liquid Chromatography/Mass Spectrometry
M_r	Relative Molecular Mass
UV	Ultra-Violet
IR	Infra-Red
m/z	Mass to charge ratio
ng	Nanogram
NMR	Nuclear Magnetic Resonance
pg	Picogram
PAHs	Polycyclic Aromatic Hydrocarbons
Pc	Critical Pressure
SPE	Solid Phase Extraction
SFE	Supercritical Fluid Extraction
SFC/MS	Supercritical Fluid Chromatography/Mass Spectrometry
SIM	Selected Ion Monitoring
TIC	Total Ion Chromatogram
Tc	Critical Temperature
TSP	Thermospray
DLI	Direct Liquid Introduction

API	Atmospheric Pressure Ionization
eV	Electron Volt
WCOT	Wall Coated Open Tubular
SCOT	Support Coated Open Tubular
RRF	Realtive Response Factors
SD	Standard Deviation
HP	Hewlett Packard
FAB	Fast Atom Bombardment
API	Atmospheric Pressure Ionization
ESP	Electrospray Ionization

CHAPTER 1

Introduction

1.1 Crude oil

Petroleum is a term derived from the Latin words petra (rock) and oleum (oil) which is used to describe a wide range of naturally occurring hydrocarbon mixtures i.e. organic compounds. A petroleum's composition consists of a complex mixture which is represented by components in the: gaseous, liquid and solid phases[1]. Petroleum deposits vary widely in their physical and to a lesser degree, their chemical properties. In spite of this the bulk of the compounds which are in crude oils are hydrocarbons i.e. compounds which only contain the elements of carbon and hydrogen. As with organic chemistry the hydrocarbons associated with crude oil can be placed into a variety of classes such as saturates, unsaturated or aromatics etc[2].

The physical and chemical properties of an individual crude oil reflects the difference in the proportions of the various classes of compounds[3].

A meeting of OPEC countries in 1983 defined crude oil in the following fashion :

"crude oil is a complex mixture of hydrogen and carbon atoms that was formed millions of years ago by sea organisms"[4].

Crude oil is a liquid which contains both dissolved gases and solids and also some solids which are suspended. The physical and chemical properties of crude oil are largely dictated by those of the hydrocarbons since they can represent up to 98% of the composition of some crude oils[1]. The other constituents of crude oils are largely hydrocarbons which contain oxygen, sulphur, nitrogen or a combination of these elements[5].

Petroleum hydrocarbons are grouped into four classes and these are as follow :

1. Paraffins (alkanes) . These are stable, saturated hydrocarbons with an increasing number of carbon atoms i.e. CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16} etc. On inspection it is observed that each of the proceeding molecular formula differs from its nearest neighbours by one carbon atom and two hydrogen atoms ($-CH_2$) and this

constitutes a homologous series[6,7] . They have the general formula $C_nH_{(2n+2)}$ and range from the simplest, gaseous methane (n=1) to very large and complex waxes, where n>100, which may have either straight or branched chain structures.

2. Naphthenes (cycloparaffins). These are also saturated, but the ends of the chain have been linked, resulting in the general formula of C_nH_{2n}. Some of the hydrogens may also be replaced by alkyl groups[8].

3. Aromatics. These are unsaturated cyclic compounds whose molecular formulae follow the Huckel rule i.e. the molecule contains cyclic clouds of delocalised pi electrons above and below the plane of the molecule, furthermore, the pi clouds must contain a total of (4n+2) pi electrons. Unsubstituted benzene represents the simplest aromatic compound[9].

4. Olefins (alkenes). These are unsaturated hydrocarbons whose non cyclic members follow the algebraic formula of $C_nH_{(2n-2)}$ and can be either straight or branched chained. Polyunsaturated alkenes are hydrocarbons which contain more than one carbon - carbon double bond.

A detailed analysis of an Oklahoma crude (performed by the U.S National Bureau of Standards) was quoted by Mckee (1956) showing 22.5% paraffins from C-5 to C-17, 9% naphthenes from C-5 to C-11, and 4% aromatics from C-6 to C-13 and this data is summarised in table 1, non- hydrocarbons and heavy residues are not included.
The proportions of each hydrocarbon class have great significance both commercially (the ratio of carbon to hydrogen has a considerable influence on burning properties) and biologically since aromatics are much more toxic than paraffins.
The chief product from an oil refinery is petrol or gasoline but the amount of high quality gasoline obtainable from crude petroleum oil by straight distillation is relatively

small and it becomes important to change some of the other fractions to make them suitable for use in commercial combustion engines[10].

In general, boiling point increases with molecular weight. Density is most influenced by molecular configuration, while viscosity depends on both. Table 2 lists some physical and chemical characteristics of typical crude oils.

The higher boiling fractions can be broken down to yield compounds which can be used in petrol, whereas the lower boiling point fractions represent the paraffins and the aromatics. Iso-octane and butyl benzene represent two important additives to petrol to improve octane rating which is related to power and acceleration characteristics of petrol engines. Generally, crude petroleum oil contains paraffins, naphthenes and aromatic hydrocarbons in varying proportions, a complex mixture ranging from gaseous to solid constituents. There are also the "asphaltin crudes" which are rich in asphalts. A petrol derived from crude petroleum might contain straight chain and branched chain aliphatic hydrocarbons, naphthenes and aromatics e.g. (benzene, toluene and xylenes) with some ethyl and methyl derivatives[11].The design of the combustion engine to give improved performance has demanded a high octane number for the petrol or gasoline, which when it was obtained simply by distillation of crude petroleum, necessitated the lowering of the end boiling point of straight run gasoline.

TABLE 1

Some characteristics of hydrocarbons in crude oil (1)

Compound	Carbon Number r	Boiling Point (°C)	Melting Point (°C)	Density (SG)	Solubility in Water	Presence in Oklahoma crude % vol
PARAFFINS						
Methane	1	-161.5		0.424	90 ml/l (20°C)	
Ethane	2	- 88.5		0.546	47 " " " " "	
Propane	3	- 42.2		0.542	65 " " "(18°C)	
Butane	4	- 0.5		0.579	150 " " (17°C)	
Pentane	5	36.2		0.626	360 ppm (17°C)	
Hexane	6	69.0		0.660	138 " (15.5°C)	1.8
Heptane	7	98.5		6.684	52 " " " " "	2.3
Octane	8	125.7		0.703	15 " " " " "	1.9
Nonane	9	150.8		0.718	c. 10 ppm	1.8
Decane	10	174.1		0.730	c. 3ppm	1.8
Undecane	11	195.9		0.741		1.7
Dodecane	12	216.3		0.766		1.7
Tridecane	13	235.6	-5.5	0.756		1.6
Tetradecane	12	253.6	6.0	0.763		1.4
Pentadecane	15	270.7	10.0	0.769		1.2
Hexadecane	16	287.1	18.0	0.773		1.0
Heptadecane	17	302.6	22.0	0.778		0.9
NAPHTHENES					"Slight"	
Cyclopropane	3	- 33.0				
Cyclobutane	4	13.0				
Cyclopentane	5	49.3		0.751		0.05
Methylcyclopentane	6	71.8		0.749		0.90
Cyclohexane	6	80.7		0.779		0.70
Methylcyclohexane	7	100.9		0.769		1.60
Ethylecyclopentane	7	103.5		0.763		0.20
Ethylcyclohexane	8	131.8		0.788		0.40
Trimethylcyclohexane	9	141.2		0.777		0.20
AROMATICS						
Benzene	6	80.1		0.879	820 ppm (22°C)	0.20
Toluene	7	110.6		0.866	470 ppm (18°C)	0.50
Ethylbenzene	8	136.2		0.867	140 ppm (15°C)	0.20
p-Xylene	8	138.4		0.861		0.10
m-Xylene	8	139.1		0.864	c. 80 ppm	0.50
o-Xylene	8	144.4		0.874		0.30
iso-Prophylbenzene	9	152.4		0.864		0.07
n-Propylebenzene	9	159.2		0.862	60 ppm (15°C)	0.09
Naphthalene	10	217.9	80.2	1.145	c. 20 ppm	0.06
2-Metyllnaphthalene	11	241.1	37.0	1.029		0.20
1-Methylnaphthalene	11	244.8	-22.0	1.029		0.10
Dimethylnaphthalene	12	262.0	-18.0	1.016		
Trimethylnaphthalene	13	285.0	92.0	1.010		
Anthracene	14	354.0	206.0	1.250		

Table 2

Some Characteristics of Crude Oils [1]

Country of origin and type	Density of SG 16 °C	Kinnematic Viscosity cSt 38 (21) °C	Wax % wt	Pour point °C	Sulpher % wt	Asphaltene % wt	Vanadium ppm	Nickle ppm	Fractions dist. Below 150 °C	Residue above 370(300) °C % wt	Pour point °C	Kinematic Viscosity cSt 38 °C	Density SG 16 °C
pennsylvania (typical)	0 811				0.081				45	(27)			
Algeria (Zarzaitine)	0.818	3.34	5.30		0.09	0.08	1.0	1.0		34.1	902	205	
Libya (Brega)	0 829	4 13	11 40	7 1	.21	.13	50*	5*		37 5	.921	410*	38
Iraq (Kirkuk)	0 845	4.75	6.5	-34	1.88	1.3				39 8	965		27
Zhran (Agha Jari)	0 854	5 60 (8 6)	7	-20	1.33	.7	18		17.9	42.7	.957		27
Iran (Gach Saran)	0 869	8.83	6.7	-12.2	1.58	1.90	107	37		47.8	.974	3583	27
Kuwait	0 869	9.6 (17)	5 5	-26 0	2.50	1.4	27	9	15.3	51.3	.975	2185	21
Nigeria (light)	0 867	5 16	8.5	-15	.19	0.05	0 8	7+		35.8	.945	1334+	43
Venezuela (Tia juana med)	0 896	25.0	4 8	-34	1.54	3.05	170	16		57.7	.974	5785	10
Cahfornia (San joaquin)	0 975				.79				4	(60)			
Mexico (Panuco)	0 988				5.18				9	(85)			

*Sarir

+Nigeria medium

1.2 Gas Chromatography/Mass Spectrometry

The combination of gas chromatography with mass spectrometry has become firmly established as a powerful technique for the identification and quantification of components within a complex mixture. Many excellent texts are available which fully describe GC/MS[12-14]. Two dominant mass analysers have emerged for GC/MS, those which are based upon quadrupole technology and those based upon magnetic deflection. Both mass analysers are capable of achieving good results for the types of samples commonly found in environmental analysis. Although faster scan rates have been reported[13] as the major advantage for quadrupole instruments, in recent years fast scanning magnetic sector instruments have been developed[15].

Despite the development of fast scanning specifications of modern magnetic sector instruments, quadrupole mass spectrometers have become the dominant means of detection. In general quadrupole mass analysers can operate at higher pressures than their corresponding magnetic sector counterparts and consequently are ideal chromatographic platforms. A major disadvantage of magnetic sector GC/MS instruments is the high initial cost and the high degree of expertise necessary to operate such systems.

A recent significant advance in GC/MS instrumentation has been the introduction of compact and low cost quadrupole mass detectors. These were pioneered by Finnigan MAT (San Jose, California, USA) in the form of the ion trap detector[16] and perhaps most successfully to date by Hewlett-Packard (Paulo Alta, California, USA) in the form of the quadrupole mass selective detector (MSD series). Since the original pioneering work, nearly all major scientific instrument manufacturers produce compact , so called "benchtop" GC/MS systems. Typical specifications of these instruments are such that full scan data is generally obtainable from several hundreds of picograms of injected sample component or even lower. Such benchtop GC/MS systems are usually only

suitable when capillary gas chromatography studies are undertaken. This limitation is a consequence of benchtop GC/MS systems not being equipped with a jet separator which is necessary when packed column GC/MS studies are undertaken[17]. The library search capability of modern day GC/MS systems as applied to mass spectra obtained by electron impact (EI) ionisation means that many individual components from a separated mixture can be potentially very rapidly identified[18]. Since many GC/MS systems make provision for chemical ionisation (CI) then the validity of electron impact library searched data can be scrutinised thus enabling a further level of confidence in positive library search results. This CI approach is particularly valuable on those occasions where the EI spectra have failed to provide molecular weight information.

The development of chromatographic methods and column selection are important aspects of GC/MS analyses, (figure 1. GC/MS block diagram) especially for samples which have been obtained from complex matrices such as crude oil. Recent gas chromatographic developments include improved injection systems and further advances in capillary column technology such as high temperature columns[19]. With capillary columns split/splitless injection techniques[20] are employed with the injection port held at elevated temperatures such that sample flash volatilisation occurs and the vaporised sample is swept onto the column by the flow of carrier gas through the injection port.

An alternative sample injection technique entails injecting the sample directly onto the top of the column which is held at a low temperature during the injection period[20]. The on-column injection technique was developed to provide maximum precision with minimum sample discrimination effects. More recently, a cold-splitless injection with a programmed temperature vaporisation device has been invented and proved to offer the same benefits as those obtained with on-column injection[21]. The major benefit of capillary gas chromatography as compared to packed column gas chromatography is that greater chromatographic resolution as achievable.

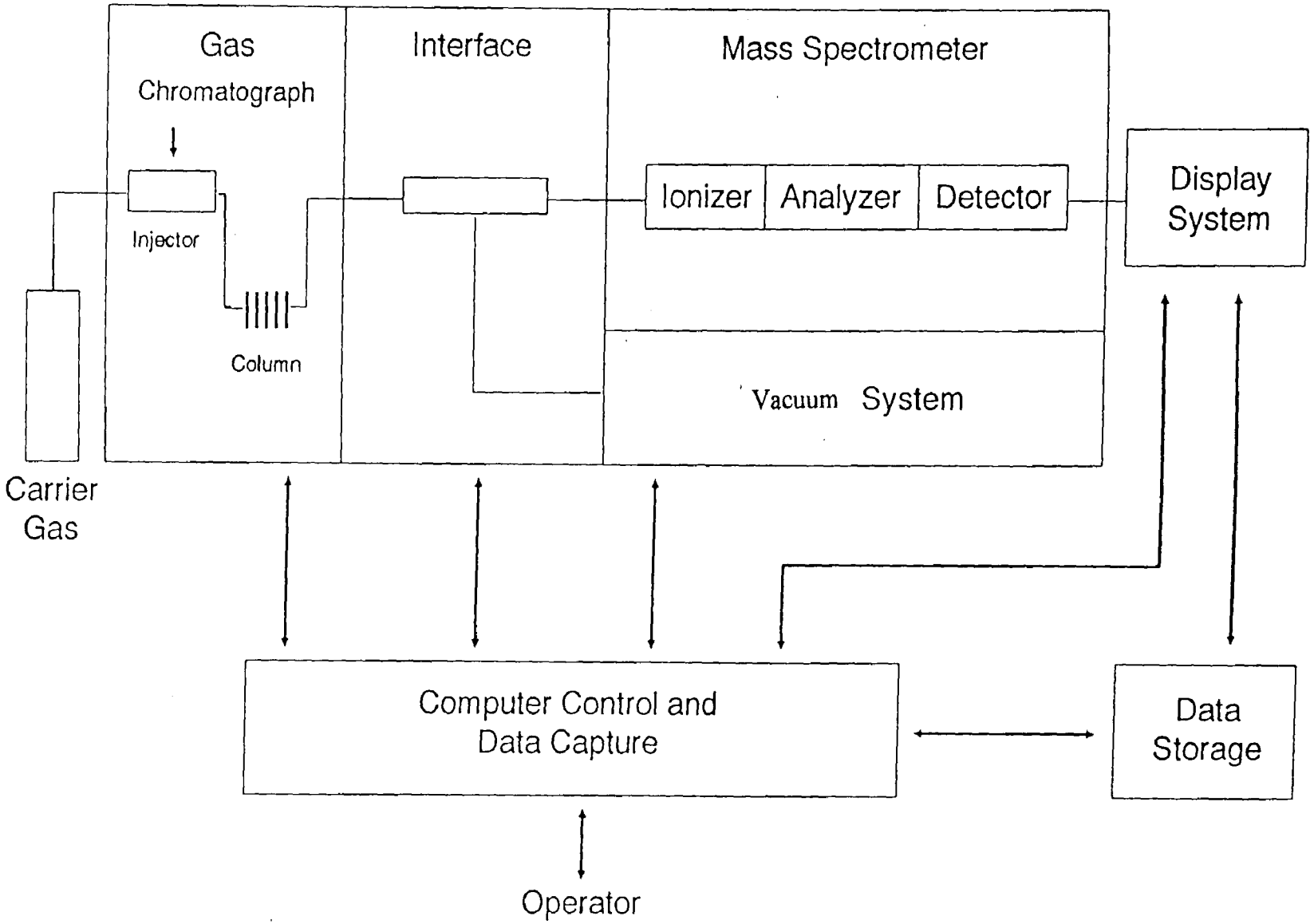


FIG 1 Block Diagram of a Typical GC/MS System

Different designs of capillary columns have been evaluated to improve chromatographic performance. GC/MS analysis using short open tubular columns has been investigated as a means to provide increased speed of analysis and enhanced sensitivity for thermally labile species such as the pesticide aldicarb[21]. Also short length, small internal diameter wall coated open tubular columns have been used to provide high resolution with increased speed of analysis for environmental samples using direct capillary GC/MS[22].

The coupling of gas chromatography with mass spectrometry has resulted in several designs of interface, this being largely influenced by the flow of gas associated with the type of gas chromatographic analysis being undertaken. In some cases the interface is such that the column is directly coupled to the ion source of the mass spectrometer, this being enabled by a heated transfer line. With this approach all of the eluent from the gas chromatograph is discharged into the ion source and this is the general means by which capillary columns are interfaced. On those occasions where packed column GC/MS studies are undertaken the gas flow from the column exceeds the pumping capacity of the mass spectrometer. Consequently the interface employed must enable the vast majority of carrier gas to be diverted from the high vacuum region of the mass spectrometer. Such interfaces generally utilise momentum as means of sample enrichment, with the jet separator [21] being a commonly encountered device alongside the heated capillary transfer line. In appropriate circumstances gas chromatography provides an excellent platform for the separation of components from a complex mixture and is easily interfaced to mass spectrometry, it nevertheless has some disadvantages. Gas chromatography is not suitable for compounds which are either thermally labile or are insufficiently volatile to be vaporised[23,24]. In appropriate cases these problems can be overcome by derivatising the sample to produce a more volatile and thermally stable species and many excellent texts cover this subject[23]. Another approach involves the

pyrolysis of the sample followed by the gas chromatographic analysis of the volatile reaction products[24]. This approach is however limited since mass spectrometry can no longer be used to confirm the presence of the original compounds.

1.3 *Combined Liquid Chromatography/Mass Spectrometry*

Unlike gas chromatography, liquid chromatography does not require the sample to be vaporised prior to analysis. Liquid chromatography has become firmly established as a means of analysing compounds which are either involatile or thermally labile. Unlike FID in GC , LC does not at present have a cheap universal detector. Mass spectrometry overcomes this problem since numerous combined liquid chromatography /mass spectrometry systems are available including a new generation of benchtop instruments[25]. The interfacing of liquid chromatographs to a mass spectrometer is more difficult than the interfacing of gas chromatographs. Typical analytical LC separations use columns which operate at flow rates of 1.0 cm^3/min and this results in gas volumes in the range 150-1200 cm^3/min depending on the mobile phase used. These volumes of gas far exceed the pumping capacity of the mass spectrometer since only approximately 20 cm^3 of gas per minute can be handled by a mass spectrometer configured for chemical ionisation. The essential features of on LC/MS interface should include the following:

(i) Should not compromise the operation of the liquid chromatograph particularly with respect to the selection of mobile phase.

(ii) Should provide good enrichment of sample.

(iii) Should provide library searchable spectra.

(iv) Should be able to maintain chromatographic integrity.

(v) Should have a high transfer efficiency between systems.

(vi) Should have a high sensitivity, comparable to that of GC/MS.

(vii) Reasonable cost.

LC/MS interfaces can be divided into two different categories[26-28]:-

(1) Those which remove the solvent prior to ionisation - such interfaces can provide EI library search capabilities.

(2) Those whose ionisation require the presence of a suitable solvent.

As a consequence of the two different categories there is no unique LC/MS interface and the different types of interface are reviewed in table 3.

Table 3. The following table shows the essential features of commercially available LC/MS interfaces[25]. Increasing numbers of stars indicating better performance.

LC/MS type *	Limit of Detection	LC flow Range	Solvent Types	Semivolatile Samples	Involatile Thermally labile samples	Mass Range
DLI	**	*	***	****	**	**
Belt	**	****	*****	*****	*	*(*)
TSP	**(**)	****	***	*****	***(*)	***(*)
LC/FAB	**(**)	*	***	****	*****	****
Particle Beam	**	**(*)	****	*****	*(*)	*(*)
ESI	****(*)	*	**(*)	****	*****	*****

1.4 *Liquid Chromatography/Mass Spectrometry Interface which remove solvent.*

Two such interfaces have been commercially manufactured, those based upon moving belt and particle beam technologies. At present the particle beam interface has largely replaced the moving belt.

The moving belt interface enables the mechanical transfer of separated components to the ion source of the mass spectrometer. Scott's studies[29] are considered the origin of current moving belt LC/MS interface. In his original work, based upon the Pye Unicam moving wire HPLC detection system[30], Scott utilised sample deposition onto a transport wire which passed through vacuum locks into the ion source of a quadrupole mass spectrometer operated in electron impact or chemical ionisation modes. A major disadvantage of using a wire as the transport platform is that it has a very limited sample loading capacity - only approximately 1% of the eluent from a conventional liquid chromatograph can be accommodated for, with the bulk being directed to waste. Another disadvantage is associated with the catalytic decomposition of sample on active sites of the wire. To overcome these disadvantages of the moving wire system, Mcfaddan et al[31] substituted the wire with a stainless steel belt whose greater surface area facilitated improved loading capacity and smoother mechanical operation of the interface[32]. In order to minimise catalytic decomposition the stainless steel belt was replaced with a polyimide belt which is an inert polymer with low affinity for many organic compounds. Figure 2 shows a schematic diagram of a moving belt interface. Several versions of the moving belt interface have been commercialised[33-35].

The moving belt interface is essentially composed of four regions :-

Region 1- Deposition of eluent onto the moving belt. This can be greatly facilitated via a thermospray nebuliser device[36].

Region 2- Solvent evaporation via an infrared heater leaving the involatile sample compounds coated to the belt.

Region 3- Two vacuum locks to protect the high vacuum of the ion source from the low vacuum region of eluent deposition and solvent evaporation .

Region 4- Sample vaporisation zone - in which the deposited sample is flash vaporised into the ion source from the belt surface. The sample is then analysed via electron impact or chemical ionisation.

Eluent or mobile phases containing a large aqueous component does not readily form a thin continuous film of solvent on the belt due to surface tension effects. A series of droplets formed on the belt surface can give rise to a " beading effect", which may lead to degradation of chromatographic integrity and cause pressure fluctuations in the ion source. The use of an aerosol spray deposition device overcomes this problem[37].

Later designs of the moving belt interface used an in electron beam directed at the tip of the belt and this has been reported to enhance sensitivity particularly for labile compounds[38] . The moving belt interface has been successfully used in the analysis of a wide variety of compounds including polynuclear aromatics[39], petroporphyrins[40] phenolics[41] and waxes[42].

The particle beam LC/MS interface is an alternative means to the moving belt interface and again since solvent is effectively removed prior to ionisation both conventional electron impact and chemical ionisation studies maybe undertaken. These interfaces have been derived from the initial studies of the MAGIC (Monodisperse Aerosol Generator for Interfacing Chromatography) LC/MS interface[43]. A typical design of a particle beam interface is shown in figure 3. LC eluent enters the device together with a flow of helium resulting in the generation of an aerosol of solvent droplets sprayed into a desolvation chamber. Within the desolvation chamber, which is held at ambient temperature and pressure, the solvent vaporises resulting in a vapour essentially composed of two components, the light solvent molecules and helium atoms and the heavy desolvated sample particles.

This mixture enters the first low pressure rotary pumped region through a narrow nozzle, a process which accelerates the gas/particle mixture, forming a supersonic jet containing a central directed beam of particles. The high momentum particles tend to remain on the axis of the separator while the light molecules tend to diffuse away. Solvent vapour and helium are "skimmed" and pumped away by a sequence of two nozzles facing the expansion jet, leaving the much heavier beam of analyte particles to travel directly into the ion source of the mass spectrometer where they strike a heated wall and are vaporised and ionized by EI or CI. The EI spectra can be searched against libraries of known spectra, an advantage this interface shares with the moving belt system. The particle beam interface can accommodate flows in the range, 0.1 - 1 cm^3/min. Originally designed for use on quadrupole mass spectrometers, it has been adapted for magnetic sector instruments[44]. The use of involatile buffers is not recommended.

The particle beam interface appears to have displaced the moving belt interface as the system of choice for compounds of medium molecular mass, largely because it has the advantages of mechanical simplicity and robustness. A source which is capable of producing either particle beam or thermospray (TSP) type spectra has been designed and is equipped with a novel solvent removal system [45] . Detection limits lie most typically in the low nanogram range. The particle beam interface is generally unsuitable for the study of high molecular mass or involatile, thermally labile material.

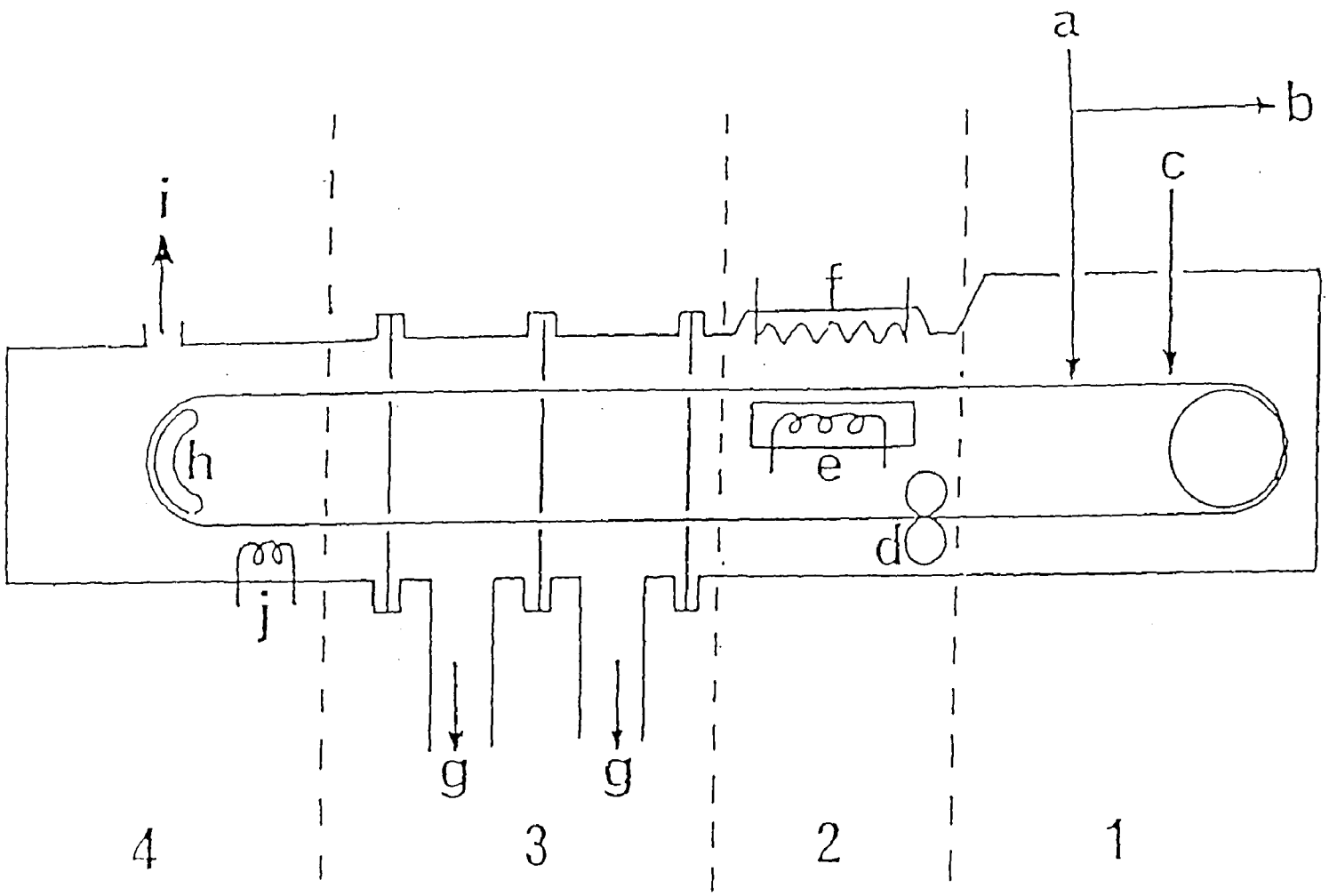
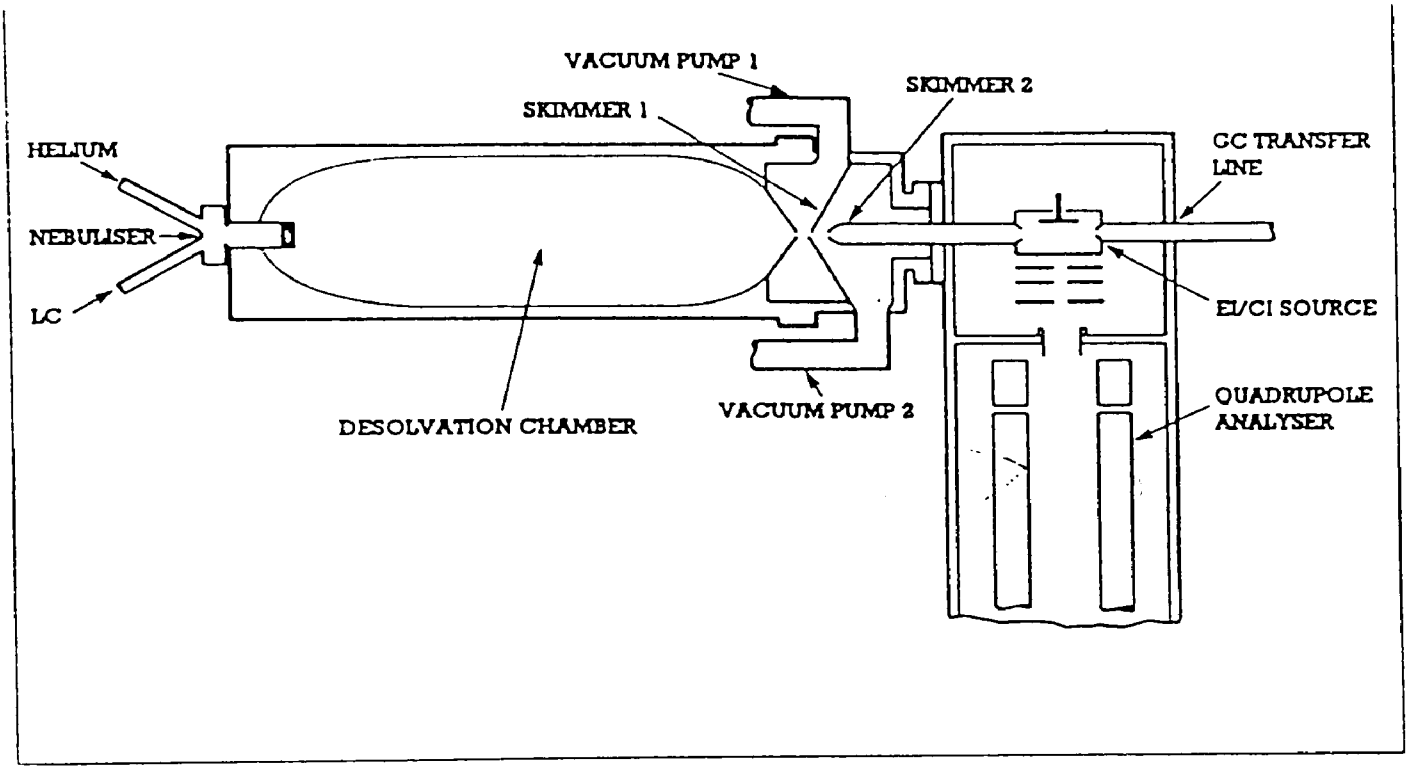


FIG. 2 Schematic of a moving belt interface.

1) Region of eluent deposition. 2) Region of solvent evaporation. 3) Vacuum locks
4) Zone of sample vaporization
a) LC flow. b) Solvent splitter. c) Co-solvent. d) Belt drive. e) Block heater
f) IR heater. g) Pumps. h) Sample vaporizer. i) Mass analyser. j) Clean-up heater.

Figure 3. Diagram of a Particle Beam LC/MS Interface



1.5 *LC/MS Interfaces where Solvent is not removed prior to Sample Ionization*

These will only be briefly described since such interfaces were not available for this project.

Direct liquid introduction (DLI) was the first example of an LC/MS interface which produced solvent mediated spectra[46]. DLI provides very poor sample transfer efficiency between the conventional liquid chromatograph and the mass spectrometer, typically only 1-2% of the eluent is introduced into the mass spectrometers ion source. Ionisation of the solvent by use of a filament results in the production of a chemical ionisation plasma and this is reflected in the spectra that are produced .

Thermospray LC/MS became the first widespread LC/MS technique[47]. It is particularly suitable for reverse phase LC/MS studies since an inorganic buffer such as ammonium acetate is required to bring about sample ionisation. Basically the eluent from the liquid chromatograph is vaporised to produce a fine stream of droplets which are sprayed into a heated desolvation chamber held under low vacuum. As the solvent starts to evaporate the droplets become smaller and statistically some of the droplets contain uneven numbers of positive and negative ions from the buffer. A point is reached when coloumbic repulsion overcomes the surface tension of the droplet and sample ions are ejected. Generally, protonated and ammonium adduct species are observed when ammonium acetate is used as the buffer[48]. A skimmer with a small orifice is located in a perpendicular position to the vaporiser jet and a small portion of sample ions are introduced into the mass spectrometers "ion source". The performance of thermospray is very compound dependent and some molecules, particularly non-polar species are not suitable for TSP LC/MS.

Continuous flow fast atom bombardment (CF-FAB) LC/MS has become firmly established as a means of providing molecular weight information for large polar

molecules. As with DLI only 1-2% of the eluent from the conventional liquid chromatograph can be handled by this interface and hence some form of splitting device is necessary when conventional LC studies are undertaken.

Electrospray ionisation (ESP) has recently become firmly established as a popular LC/MS technique such that a benchtop system is commercially available[25]. ESP is particularly suitable for reverse phase systems and is rapidly replacing thermospray LC/MS. In ESP an acid such as formic acid is incorporated into the LC eluent. The LC eluent is fed to a capillary and situated in front of this there is an electrode held at high potential. The eluent becomes nebulised under the influence of the strong electrostatic field and is directed towards a series of skimmers housed in an evacuated chamber. Polar samples become associated with protons from the LC eluent and eventually the protonated and desolvated sample molecules are introduced into the mass spectrometer for mass analysis. ESP can produce multiply protonated sample molecules and can therefore greatly extend the mass range of the mass spectrometer[25,36,49,50].

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CHAPTER 2

The use of Commercial Solid Phase Extraction Cartridges for the Fractionation of Crude Oils

2.1 *Introduction*

Solid phase extraction (SPE) has become a firmly established technique for the rapid and selective sample preparation for a wide variety of matrices [1]. SPE offers a faster, more cost effective sample preparation method with dramatic time savings over many traditional liquid/liquid extraction techniques. SPE is based on specific molecular interactions for more reproducible results[2]. In principle SPE offers an attractive alternative to the fractionation of crude oil by column chromatography[3,4] which would automatically entail the use of relatively large volumes of toxic and flammable organic solvent as hexane and benzene.

SPE offers many other benefits and advantages over traditional sample preparation techniques, such as liquid/liquid extraction, and these are listed as follows[5]:

1- Extracts of high purity can be isolated.

2- Simple ease of use.

3- Target analytes can be isolated with high recoveries.

4- In appropriate cases SPE offers the analyst an important means of concentrating trace levels of analytes.

5- SPE procedures can be automated.

SPE is a relatively simple technique to use, employing inexpensive, disposable extraction cartridges that are available in a wide range of sizes with a variety of sorbents. In principle, SPE is analogous to liquid/liquid extraction - as the liquid sample passes through the SPE column, compounds are extracted onto the selected sorbent. Extracted compounds may then be isolated by passing aliquots of solvent through the cartridge and at this stage the analyst may develop an appropriate solvent fractionation system such that a highly purified extract maybe obtained. An example of a typical extraction procedure is illustrated schematically in figures 1 and 2.

The objective of this section was to develop an SPE method for the fractionation of crude oil such that the aromatic species would be isolated from saturated hydrocarbons. In order to facilitate this investigation a method was first developed using PAH standards only, and in order to assess the utility of the method it was decided that recoveries of each PAH should be determined by quantitative GC/MS.

2.2 *Quantitative GC/MS*

GC/MS is unique in the ability to quantify trace levels of specific compounds in highly complex matrices. Quantitative GC/MS is also characterised by a wide dynamic range for the analysis of target analytes[6]. Quantitation is achieved by the selection of target ions specific to the analytes of interest whose responses are integrated and compared with those of standard solutions which are used to construct a calibration graph. In order to minimise errors associated with fluctuations in instrument sensitivity over the analysis period along with errors associated with sample injection techniques an internal standard is generally incorporated during the preparation of the samples. The most effective internal standards are isotopically labelled analogues of the compound being analysed [7]. Such compounds have the same chemical and physical properties as the corresponding analytes and as such coelute with the analytes of interest thus affording a high degree of confidence in the final result which may otherwise be influenced by slight variation in instrument sensitivity during the analysis. Isotopically labelled internal standards tend to be expensive and hence non-labelled standards with different retention times are frequently used as an economic alternative.

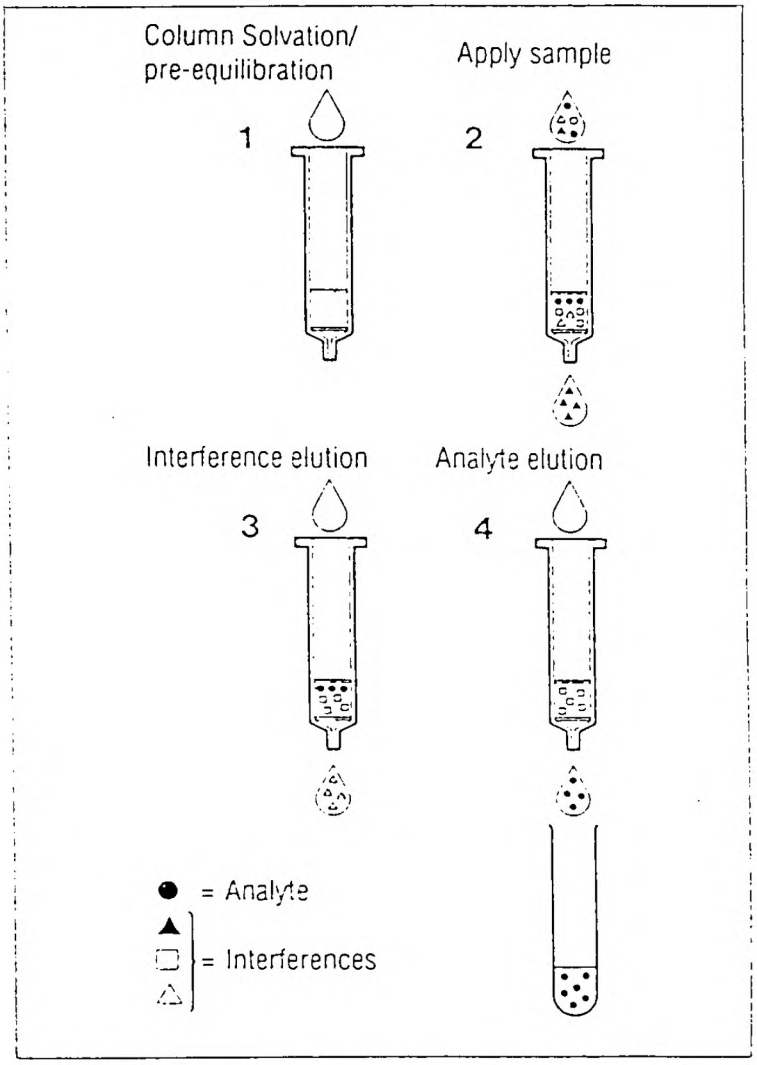


Figure 1. Atypical extraction procedure

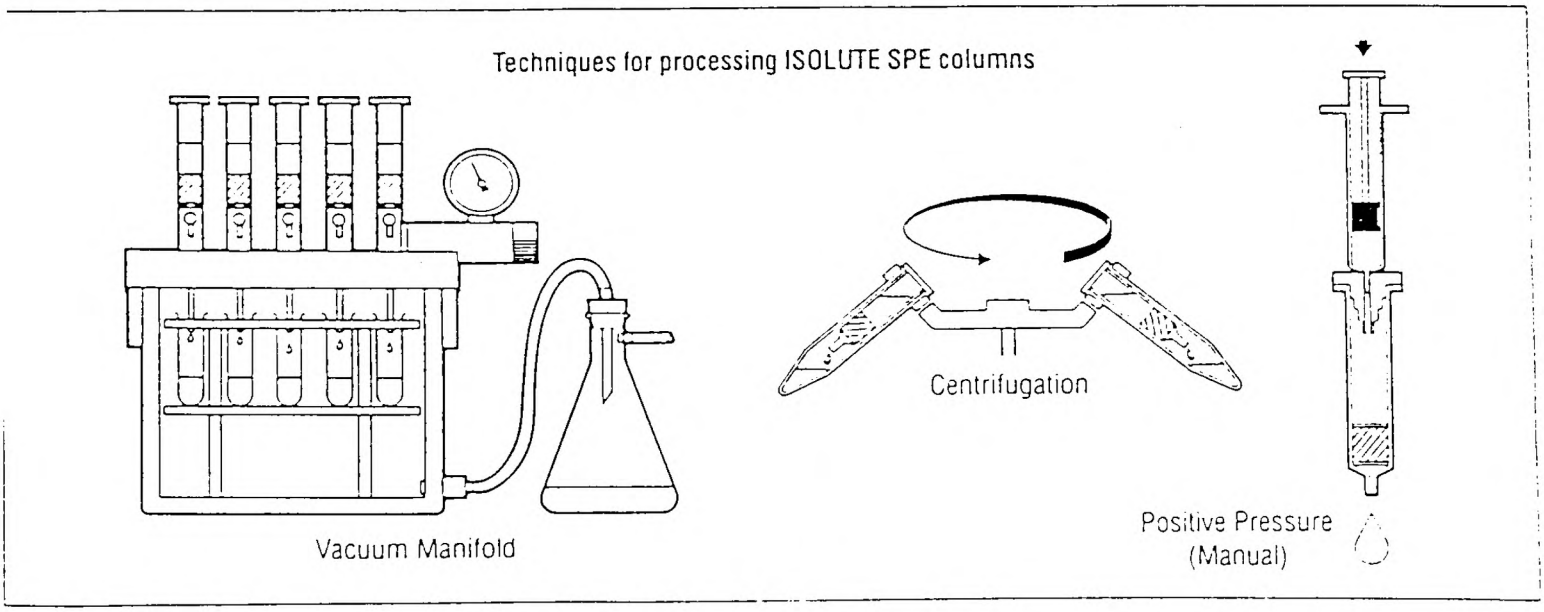


Figure 2. Techniques of types of processing methods which are commonly employed.

Quantitative GC/MS can be performed in either full scan mode or selected ion monitoring the (SIM) mode, the former permits unequivocal confirmation of the result whilst the later approach enables detection limits to be greatly improved. The SIM technique is very useful for quantitative studies in which stable isotope analogues are used as internal standards[8].

Recent developments in quantification software programs include retention time filters along with qualifier ions which are unique to the specific target compound.

Many applications of trace level residue analyses by quantitative GC/MS have been reported[9,12].

2.3 *Development of an SPE method for the quantitative recovery of PAHs*

Bondelut (Varian, UK) silica and cyano SPE cartridges were used. In order to estimate the recoveries of PAHs known quantities of these analytes were applied to a cartridge system and the appropriate fractions were analysed by quantitative GC/MS.

Hypersol grade hexane, benzene and methanol (BDH, Kernick Scientific, UK) were used as solvents for extracting the PAHs from the SPE cartridge system.

The SPE cartridges were first conditioned with hexane in accordance with the recommended procedure[13]. The silica SPE cartridge was then inserted into the top of the cyano SPE cartridge[14]. A known volume of the standard PAH solution was then applied to the silica cartridge and the extraction procedure that was developed is summarised in figure 3.

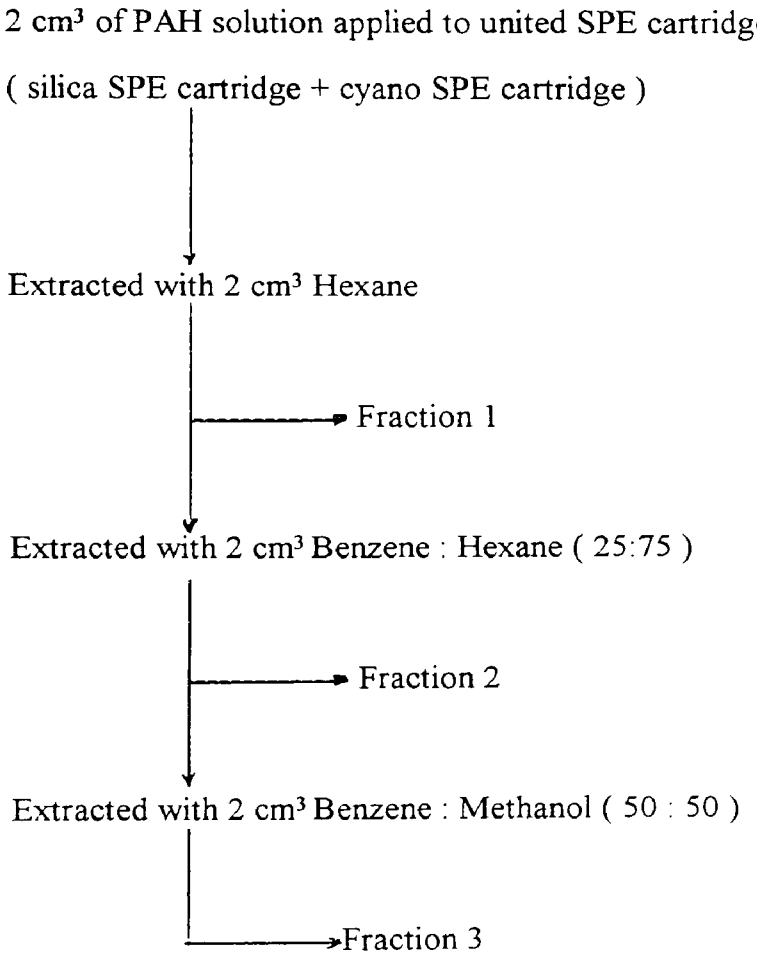
Each of the three fractions were rapidly screened for the presence of PAHs by placing a 1ul spot of each solution on a filter paper which was then placed under a ultra-violet lamp at 254 nm. The second fraction gave an intense UV response however both fractions one and two were later subjected to GC/MS analysis to confirm the validity of this rapid screening procedure. Fraction two was then blown to dryness under a stream

of nitrogen and this extract was then redissolved in $2cm^3$ hexane with 50 ppm of pentadecane as internal standard. Recoveries of the individual PAHs were then calculated by analysing the solution of fraction two by quantitative GC/MS. In order to facilitate this individual PAH, GC/MS calibration graphs had to be constructed.

2.4 *Determination of the recoveries of PAHs by Quantitative GC/MS*.

The full scan mass spectra of the individual PAHs are included in the appendix. In electron ionisation the mass spectrum of each PAH is dominated by a molecular ion as base peak and little fragmentation is observed. All of the EI PAH mass spectra also show the formation of a doubly charged molecular ion species. In order to facilitate the construction of a GC/MS calibration graph three standard solutions containing identical amounts of internal standard were prepared. The three standard solutions contained diffrent known amounts of each PAH. These solutions are referred to has high, medium and low. In order to help minimise errors associated with experimental manipulations all standard solutions and spike solutions were made from a central stock solution of the PAHs dissolved in hexane. Each standard solution was prepared by carefully withdrawing an appropriate volume of stock solution, evaporating to dryness under a stream of nitrogen and then making up to exactly 2 cm^3 via a 50 ppm hexane solution of pentadecane which served as internal standard. Details of the compositions of these standard solutions are shown in table 1. GC/MS analyses were conducted in full scan mode. Ions selected for the construction of a calibration graph for each individual PAH are shown in table 2 . The target ions of each of the analytes and internal standard were extracted and integrated over a one minute retention time filter whose length was experimentally determined. The retention time filter is normally centroided around the experimental retention times.

Standard PAH solution



*Hexane solution containing 100 ppm each of Naphthalene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene and Chrysene.

Figure 3. SPE Procedure for the analysis of PAH standards.

Response Factors (area of compound / area of internal standard) were calculated automatically using the Hewlett Packard software. The relative response factors (RRF) and standard deviation (SD) or Corr. Coeff. are also calculated for each compound from the calibration graphs. Examples of the calibration graphs obtained from the PAH standard solutions are shown in figures 4-6.

With the notable exception of naphthalene satisfactory calibration graphs were constructed for all of the PAHs. Naphthalene was not detected in either of the medium or low standard solutions and was only barely detected in the high solution. This is attributed to naphthalene being very volatile such that significant losses were most probably incurred during the blowing down stage as previously described for the preparation of the standard solutions.

In order to assess the recoveries of the individual PAHs from the solid phase sorbent system, 2 cm^3 of the hexane PAH stock solution were applied to the linked SPE cartridges. Figure 7 shows the GC/MS analysis of the standard PAH solution (does not contain internal standard). Details of the extraction procedure employed have been previously shown in figure 3. The SPE (fraction two) containing the PAHs was blown down to dryness and then redissolved in 2 cm^3 of the pentadecane solution prior to GC/MS analysis. Individual PAH target ions were integrated and the percentage recoveries were automatically calculated via the quantitative GC/MS software programme. The recoveries of the individual PAHs are shown in table 3.

Figure 4- Calibration graph for quantification of Fluorene

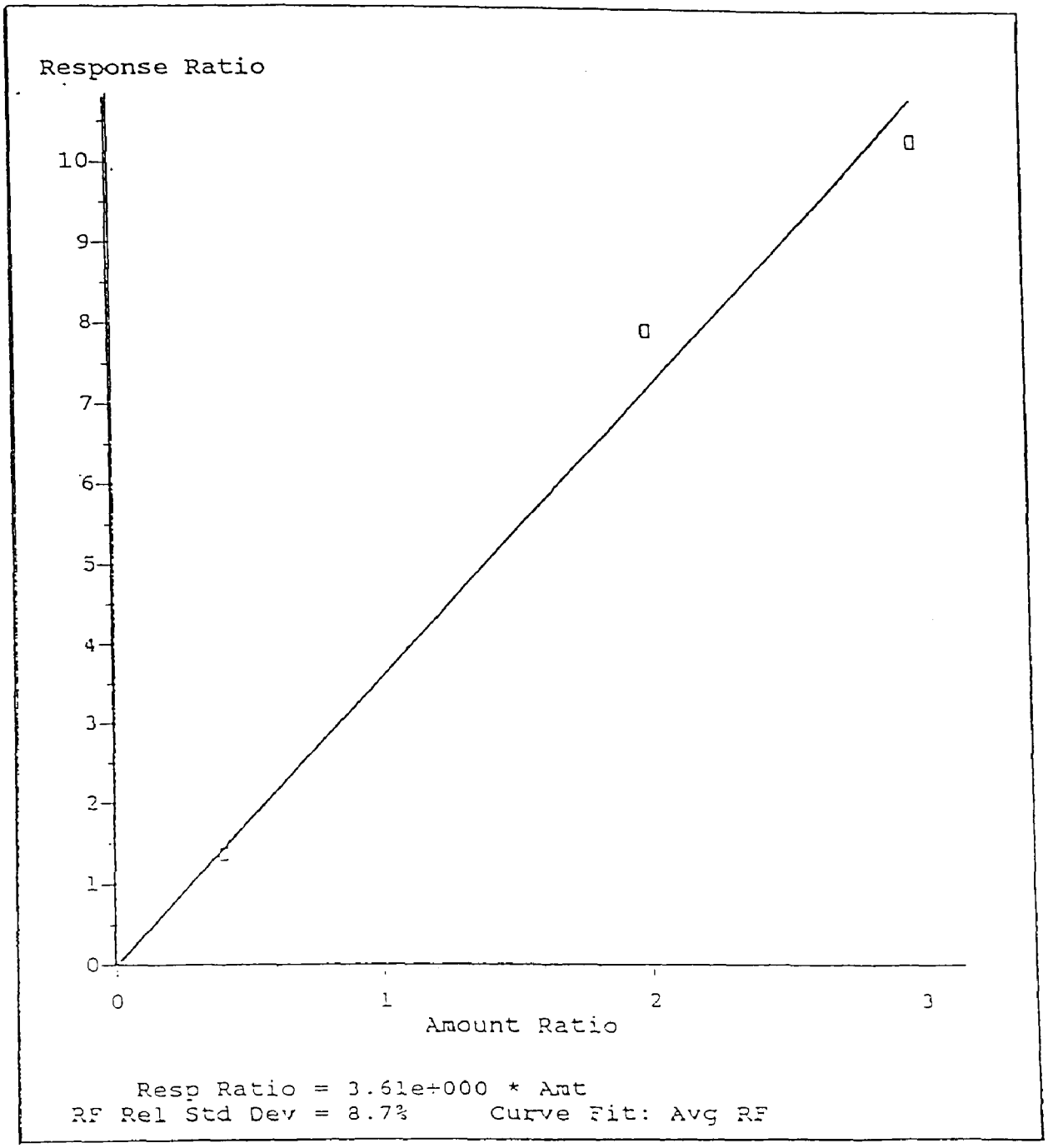


Figure 5- Calibration graph for quantification of Phenanthrene

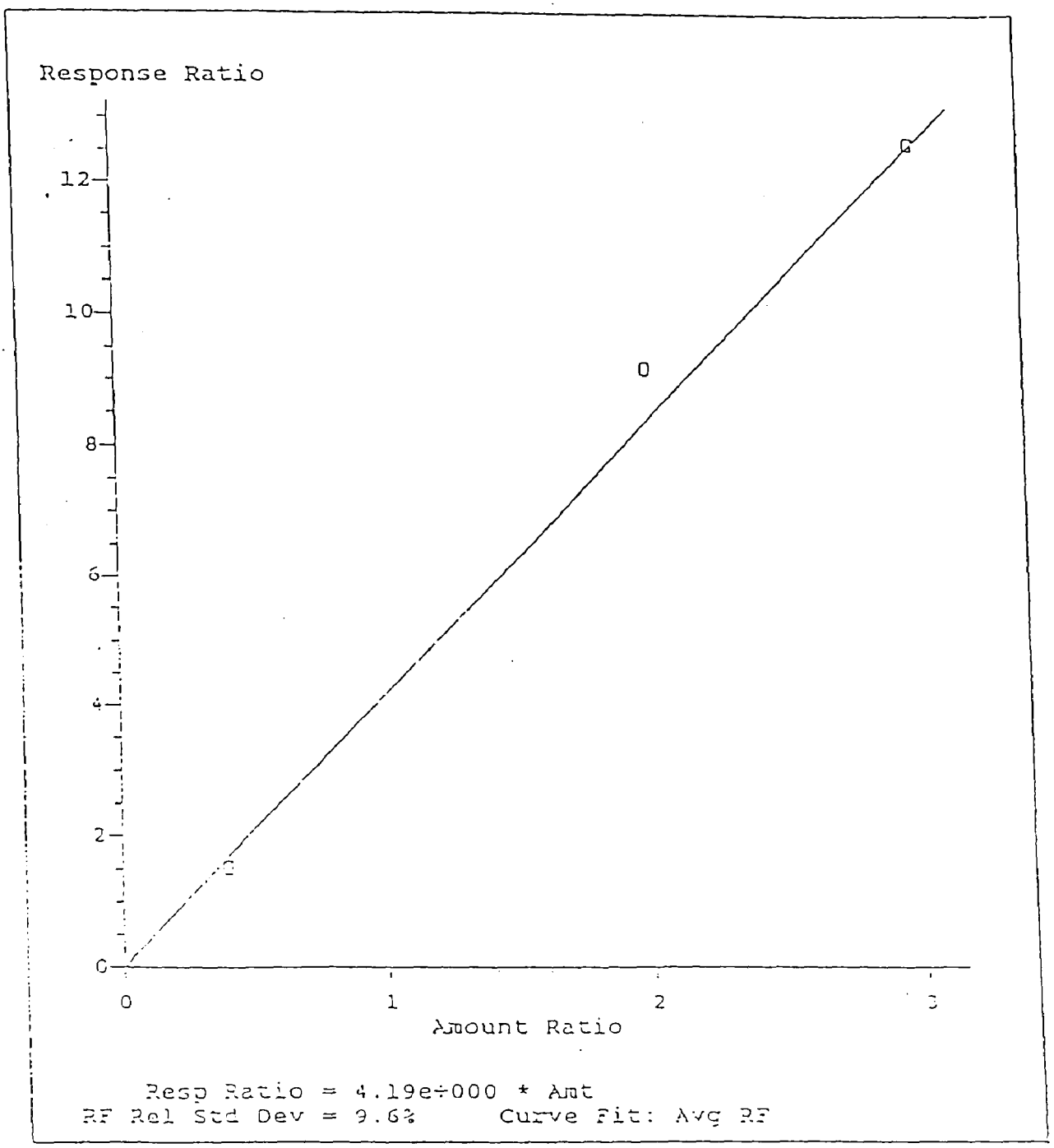


Figure 6- Calibration graph for quantification of Anthracene

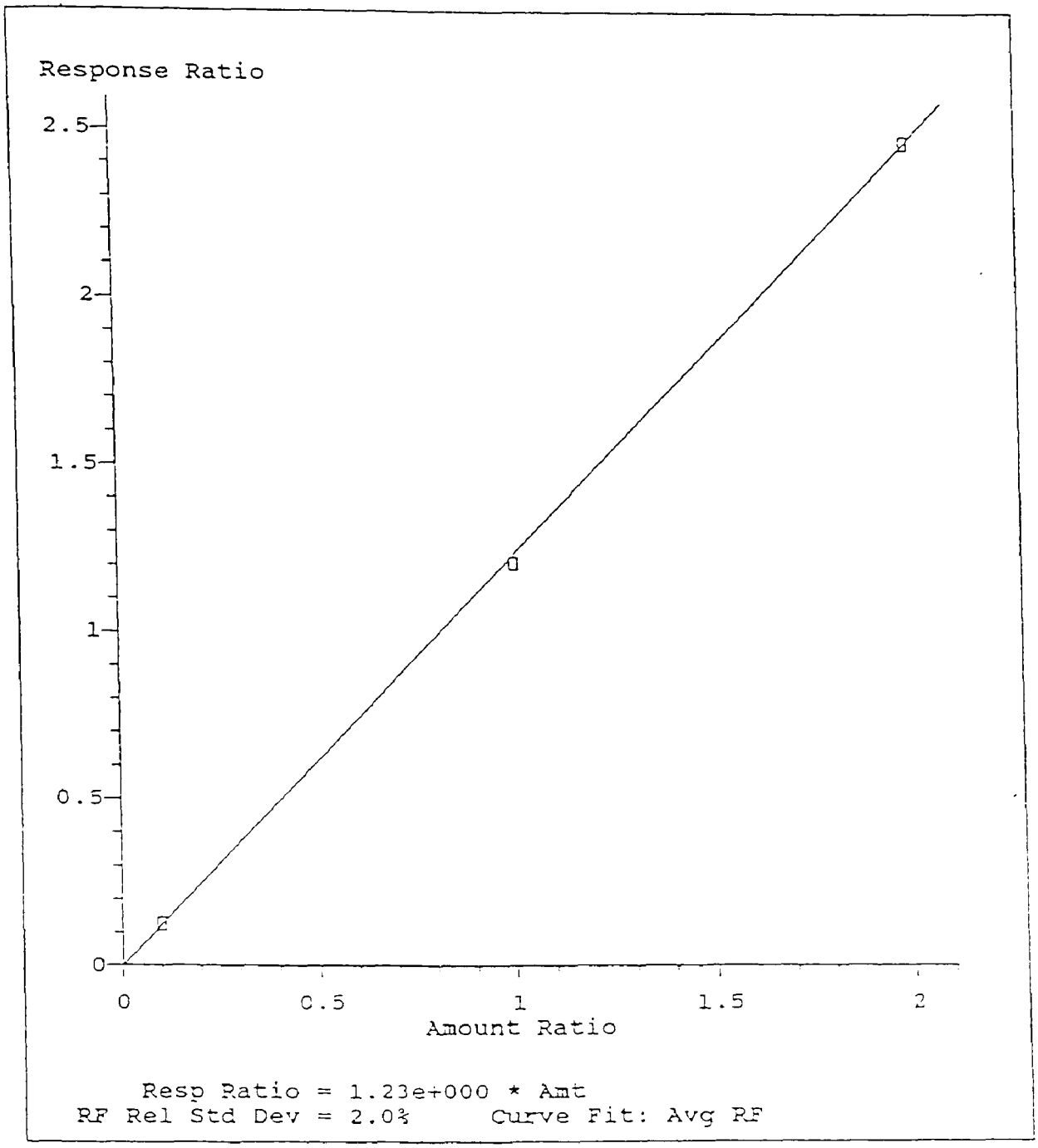


Table 1. Composition of Standard Solution for quantitative GC/MS. Values quoted in ppm.

Concentration	Low	Medium	High
Fluorene	20	100	150
Phenanthrene	20	100	150
Anthracene	10	50	100
Fluoranthene	20	50	100
Pyrene	10	50	100
Chrysene	10	50	100

Table 2. A list of target ions for each analyte and internal standard.

Analyte	Target Ions	Retention time
Naphthalene	128	7.95 min
Internal Standard	212	10.63
Fluorene	166	13.48
Phenanthrene	178	15.82
Anthracene	178	15.93
Fluoranthene	202	18.86
Pyrene	202	19.37
Chrysene	228	22.45

Table 3. Recoveries of the individual PAHs following SPE fractionation.

Peak	Compound	Retention time	Recoveries
1	Internal standard	10.63	--
2	Fluorene	13.48	95
3	Phenantrene	15.82	96
4	Anthracene	15.93	107
5	Fluoranthene	18.86	105
6	Pyrene	19.37	102
7	Chrysene	22.45	98

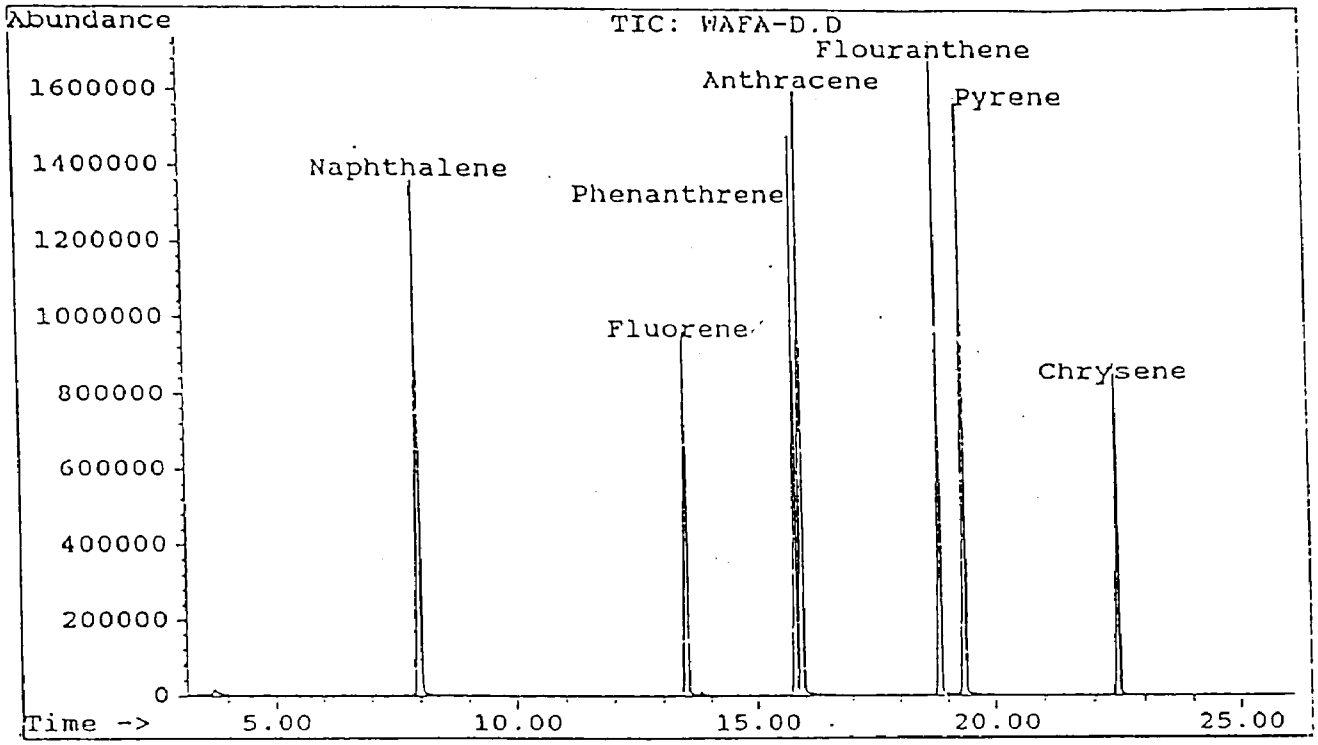
2.5 *Asphalt*

Asphalts represent a class of compounds in crude oil which are composed of many aromatic rings. The larger aromatic hydrocarbons in crude oil are divided into two classes on the basis of their solubility in pentane. Those compounds of asphalt that are soluble, are classified as resins,whereas those which are insoluble are called asphaltenes[15].

Asphalt is a dark brown to black material in which the predominant constituents are bitumens which contain very high molecular weight hydrocarbons called asphaltene and aromatic and chlorinated hydrocarbons. Since the early nineteen hundreds most asphalts produced from the refining of crude oil have been primarily used in paving and roof applications[16].

Asphaltenes were removed from the oil sample by allowing on oil-solvent solution to stand at room temperature for one hour followed by centrifugation for 15 minutes[17].

Figure 7- GC/MS analysis of the standard PAH solution. This solution was used to estimate the recoveries of individual PAHs from the SPE procedure.
GC/MS conditions given in the appendix.



2.6 *SPE Fractionation of Libyan Crude Oil*

The objective of this work was to evaluate the SPE methodology used in the isolation of a PAH spike as previously described in section 2.1, for the fractionation of crude oil into four different classes of compounds i.e. saturates, aromatics, resins, and asphaltenes. Approximately 38 mg of crude oil were dissolved into 2 cm^3 of hexane solution and this was then applied to the coupled SPE cartridge system and extracted as described previously in section 2.3. Both blank SPE cartridges had been weighed carefully in order that the mass of asphaltenes in a given mass of oil could be estimated. All SPE solvent fractions obtained were then analysed by full scan electron ionisation GC/MS.

The GC/MS analysis of fraction one is shown in figure 8. Inspection and library searching of the associated mass spectra revealed that fraction one was composed of saturated hydrocarbons and that no aromatics had been detected. The chromatogram for fraction two is shown in figure 9. Analysis of the spectra again revealed that no aromatics could be detected and like fraction one, fraction two was largely composed of saturated hydrocarbons. Ion chromatography also failed to detect the presence of any PAH species in the second fraction. Using the SIM procedures developed for the PAH standards, only naphthalene and chrysene could be identified in SPE fraction two obtained from Libyan crude oil. The SPE cartridges were air dried until a constant mass was obtained and following the SPE methodology it was estimated that the Libyan crude oil sample was composed of approximately 5% asphaltenes by weight.

The results failed to match our expectations following the development of the SPE methodology in section 2.3 which was successful for the high recovery of PAHs from a standard solution. Following the above results it was decided to fractionate a Libyan crude oil sample which would be spiked with several PAH standards. This experiment was undertaken to assess whether the crude oil itself was behaving as a solvent which in turn modified the extraction protocol.

Figure 8. GC/MS analysis of SPE fraction one (see figure 3) obtained from Libyan crude oil. GC/MS conditions given in the appendix.

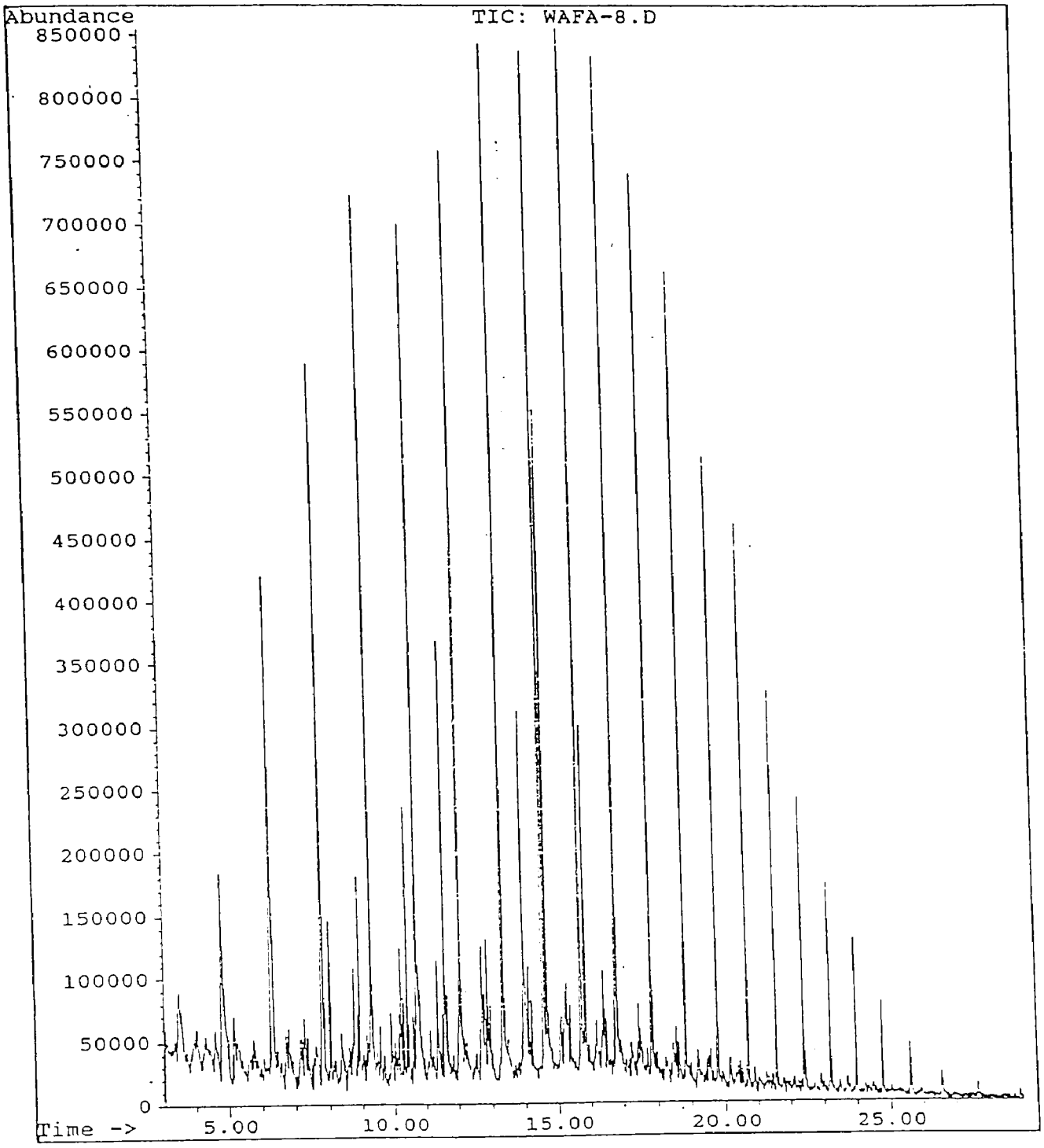
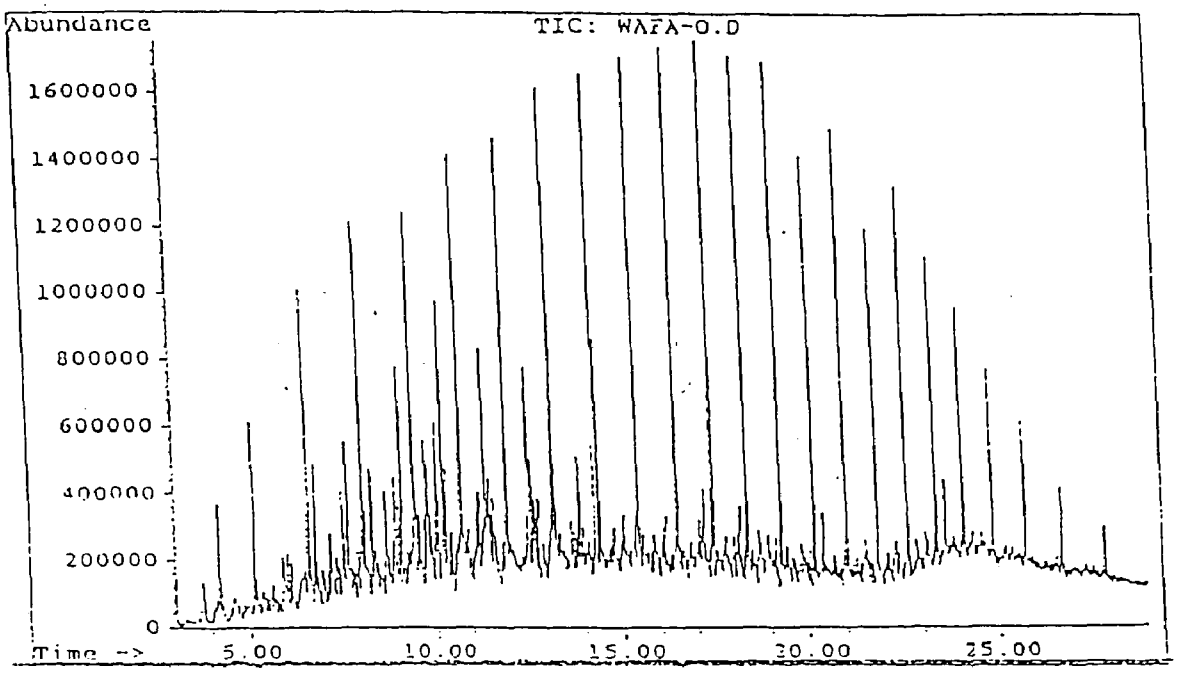


Figure 9. GC/MS analysis of SPE fraction two (see figure 3) obtained from Libyan crude oil. GC/MS conditions given in appendix.



The results of these experiments are summarised through figures 10-11. As can be seen the PAH standards were detected in both SPE fractions one and two at significant levels.

In order to finally confirm whether the crude oil itself was acting as an organic modifier the same PAH spike in isolation was applied to an identical SPE cartridge system and "fractionated" in an identical fashion. The fractions thus obtained were again analysed via GC/MS. The vast majority of the PAH standards were present in SPE fraction two, see figure 12, and only by very greatly multiplying the individual ion chromatograms appropriate for the molecular ions of the individual PAH standards could trace quantities of the PAH standards be found in SPE fraction one.

Figure 10. GC/MS analysis of SPE fraction one (see figure 3) obtained from PAH spiked Libyan crude oil. GC/MS conditions give in the appendix.

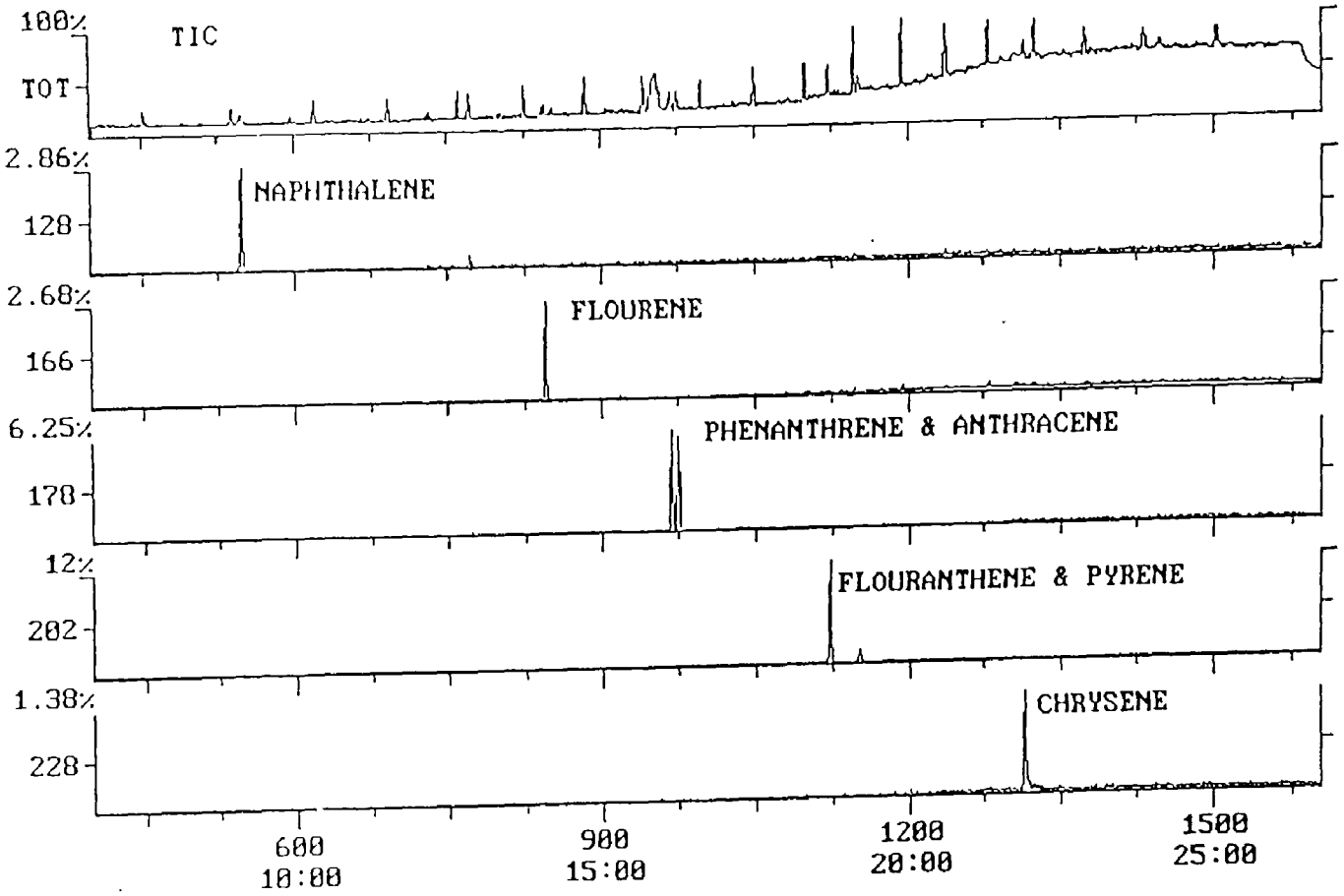


Figure 11. GC/MS analysis of SPE fraction two (see figure 3) obtained from PAH spiked Libyan crude oil. GC/MS conditions give in the appendix.

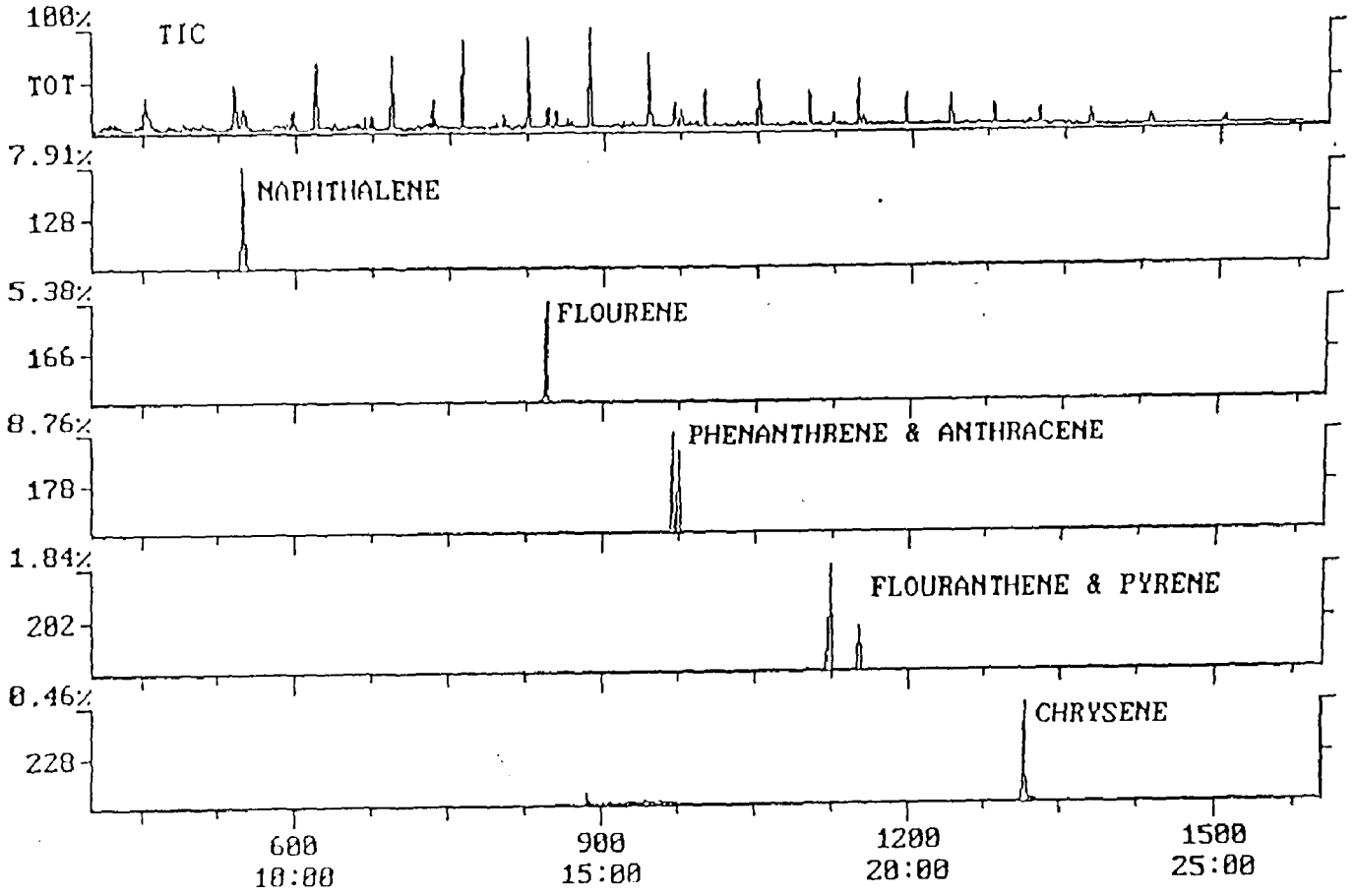
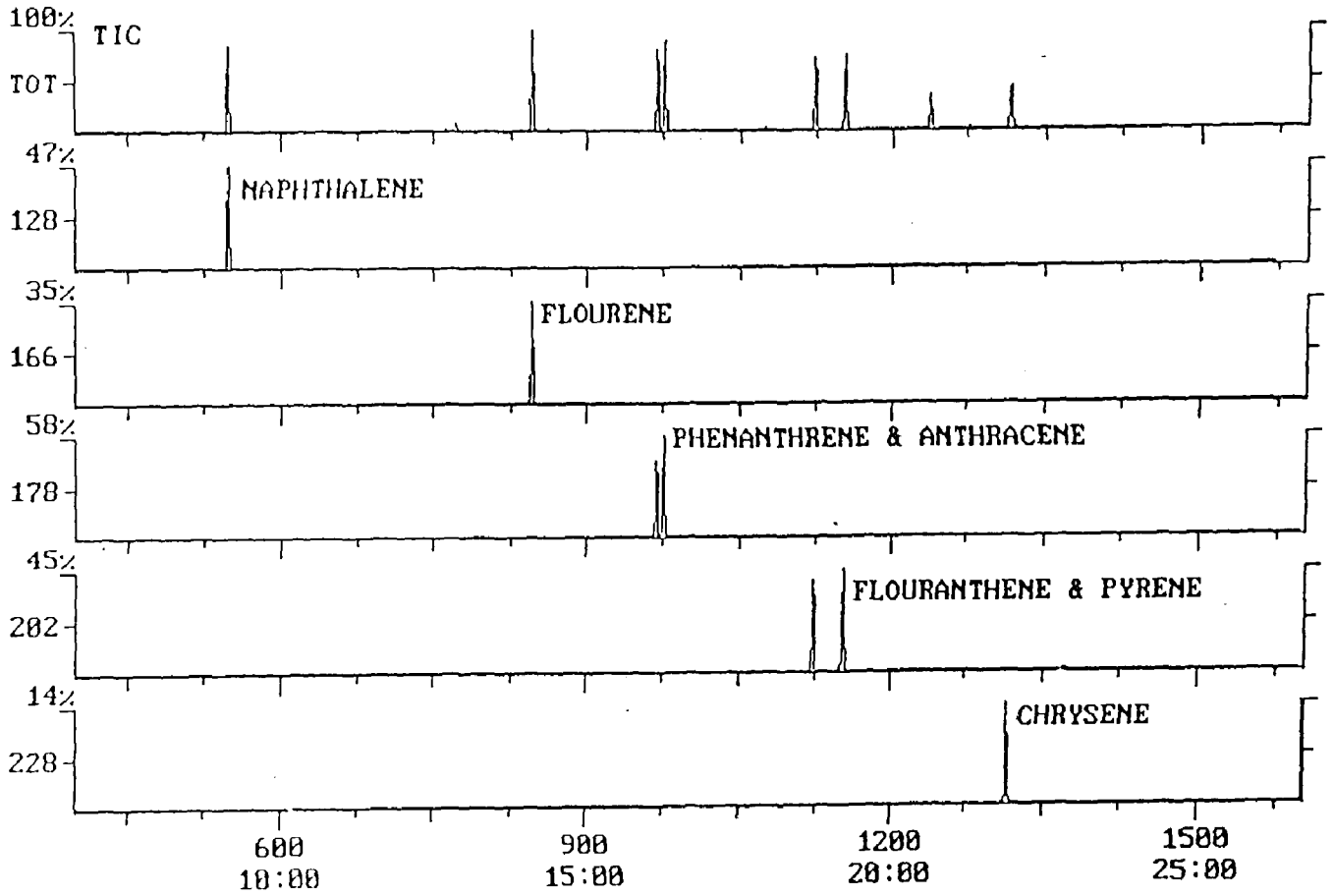


Figure 12. GC/MS analysis of SPE fraction two obtained from the PAH solution used to spike Libyan crude oil. GC/MS conditions give in the appendix.



2.7 *Discussion of The SPE Results and Methodology*.

Although a satisfactory SPE procedure had been developed for the high recoveries of individual PAH standards from a coupled SPE cartridge system, the method was largely unsuccessful when applied to the analysis of crude oil. The SPE method did not provide a fraction which could enable the aromatic profile of crude oil to be determined by full scan GC/MS. When the crude oil fraction thought to contain the PAHs (SPE fraction 2) was analysed via SIM GC/MS, only two PAHs could be identified.

It seems likely that at the level of loading crude oil onto the SPE cartridge, the crude oil itself acts as a solvent modifier for the SPE method. This conclusion was arrived at following significant levels of detection of PAHs in fractions one and two produced from the fractionation of PAH spiked crude oil. Another possible contributing factor to this experimental observation is that the SPE cartridge may have become overloaded with crude oil.

In order to investigate these conclusions it was decided that scale- up procedures using column chromatography would be required in order to investigate the following :

1. If Libyan crude oil contained only low quantities of aromatic species, resulting in dilute SPE fractions for GC/MS analysis, then scaling-up via column chromatography should help overcome this problem.

2. Sample/stationary phase loading relationships can be more easily studied using a scaled-up fractionating procedure.

3. If the fractionation of crude oil by column chromatography proved to be successful in providing a method whereby the aromatic constituents be identified by full scan GC/MS, then the SPE fractions could be reanalysed via SIM GC/MS. Such further analysis would require the modification of the PAH SIM file to make provision for the detection

of PAHs other than the standards. This approach seems valid since SIM analysis of an SPE fraction of unspiked crude oil did result in the detection of two PAHs.

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CHAPTER 3

Fractionation of Crude Oil by Column Chromatography

3.1 *Principles of Column Chromatography*

Chromatographic techniques are classified according to their practical rather than their theoretical basis[1,2,3]. All forms of chromatography require at lest two immiscible phases, one static and the other mobile. Most often the stationary phase is a solid or a liquid held on a solid support and the mobile phase is most commonly a gas or a liquid. All chromatographic separations are the outcome of the sequential, differential partioning of the components within a mixture between the stationary and mobile phases.

An introduction to column chromatographic procedures can be aided by a preliminary description of two basic types of system in popular use. A glass tube, normally positioned vertically, is packed with particles of the stationary phase, which rest upon a rigid porous support e.g. glass-woolpad, at the bottom of the tube, to prevent further movement of the stationary phase in a downward direction[4], see figure 1. The space between the particles is completely filled with a liquid which moves under the influence of gravity and can pass out at the bottom through the porous support.

A solution of the mixture of substances to be separated, dissolved in a small volume of the liquid phase, is added just above the top of the stationary phase and is allowed to draw in. When the liquid has fallen to the top of the stationary phase, the empty upper portion of the tube is filled with a further quantity of the eluting solvent (mobile phase) and, if the separation requires a substantial volume of solvent a reservoir is connected to the top of the tube, directly by means of flexible tubing.

This provides a means of controlling the rate of flow of the moving phase through the column, see figure 2. Initially, the substances to be separated are mixed together in a layer at the top of the column, see figure 1 (a). As the elution proceeds, the fastest moving substance (i.e lowest affinity for the stationary phase) travels ahead of the others and passes down the column as a sharp but steadily broadening band or zone see figures 1 (e) - (g).

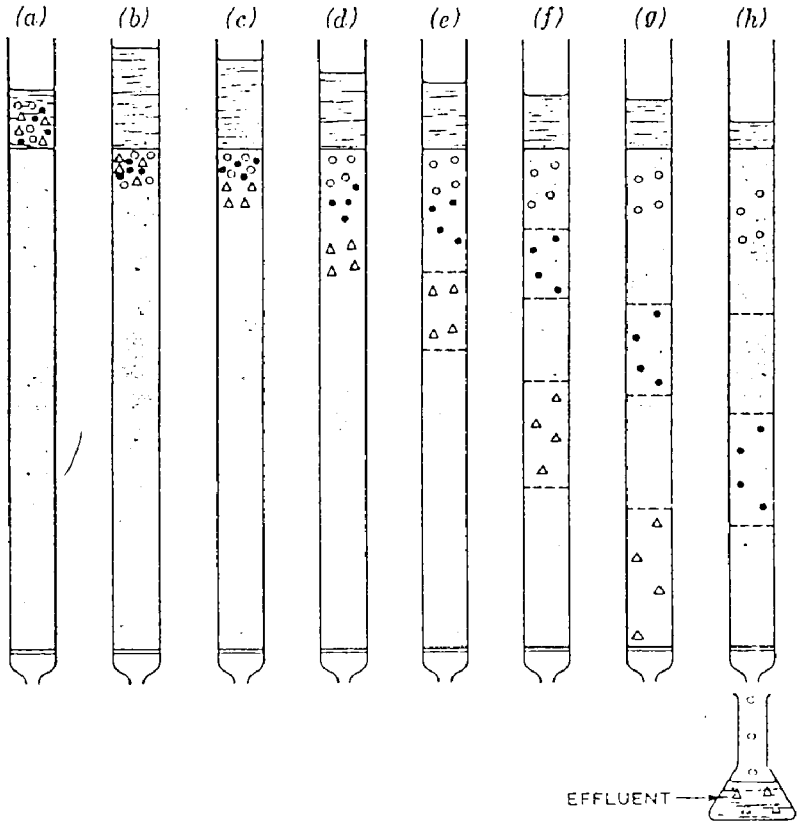


Figure 1- Separation of the components of mixture by column chromatography. The mixture of substances added in solution percolates into the top of the column of stationary phase (a), more solvent is then added (b). The different substances travel down the column at different rates (b) to (h). A distinct zone of the fastest moving substance (represented by triangles) has become separated at (e) and appears in the effluent at (h). This will be followed by pure solvent before the second component (black circles) emerges[4].

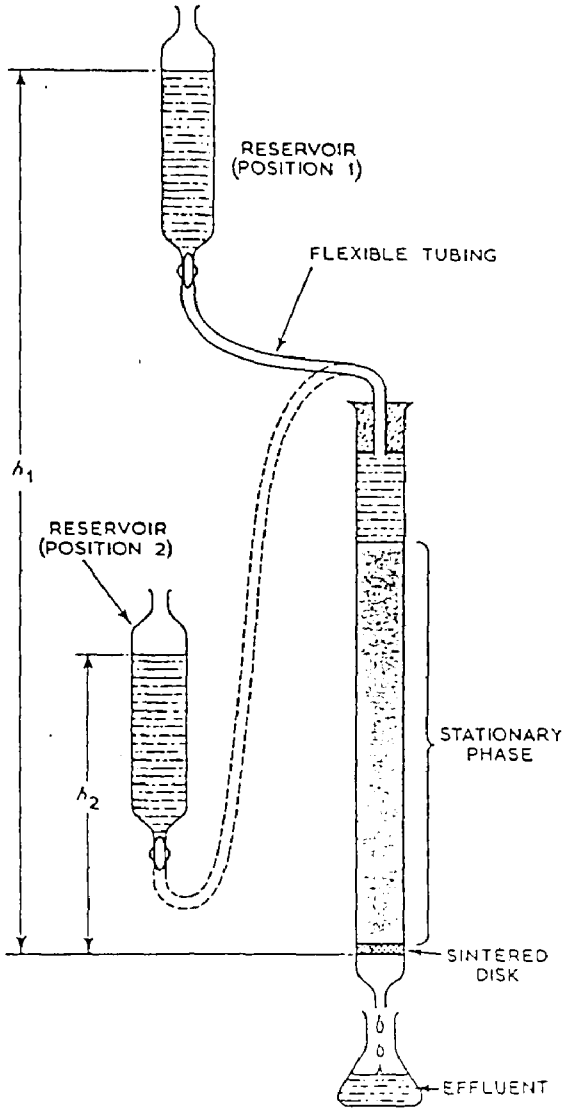


Figure 2- Chromatography column with solvent reservoir connected by flexible plastic tubing. The moving phase flows past the stationary phase which forms a column in the vertical tube. The rate of flow due to gravity is proportional to the height (h) of the meniscus of the liquid in the reservoir above the sintered disk at the base of the column. By lowering the reservoir from position 1 to position 2 (which may be below the top of the column) the flow rate is decreased in the ratio h2 to h1[4].

Heavy petroleum oil, coal liquid and oil sand bitumen have been separated into four fractions through a silica column, with good recovery and repeatability[5]. Fractionations were carried out as described[6,7] using a sample/gel ratio about 1/25.

3.2 *Fractionation of Libyan Crude Oil*

The Libyan crude oil to be subjected to column chromatography was withdrawn from the identical stock which was used in the SPE studies described in Chapter two. Initial pilot column chromatography studies were undertaken using a 50 cm^3 burette as the column. The burette was dry packed with 25g of silica of 0.13-0.25 mm particle diameter (BDH, Poole, England) with a wadding of glass wool acting as support. This packing arrangement resulted in a column of silica whose length was approximately 32 cm and whose diameter was 1.2 cm. The column was first conditioned by passing 50 cm^3 hexane under gravity feed, 1g of Libyan crude oil dissolved in 50 ml of hexane was then applied to the column and this application procedure produced fraction one. The second crude oil fraction was obtained by passing 50 cm^3 of hexane:benzene (75:25) through the column. The third and final fraction was obtained by passing 50 cm^3 of benzene:methanol (50:50) through the column. Each of the three fractions thus obtained were blown down to dryness and redissolved in 2 cm^3 of hexane and these solutions were then analysed by GC/MS. The results of the GC/MS analyses revealed that fraction one primarily consisted of saturated hydrocarbons. The GC/MS analysis of fraction one is shown in figure 3 and it became apparent that several aromatic species could be identified. The third fraction gave a relatively weak chromatogram with no aromatics being detected. The strong brown coloration of the third fraction probably arises from the presence of involatile resin species. The column was air dried and weighed and these results indicated that the crude oil consisted of approximately five percent of asphaltenes as previously determined from the SPE studies. Most importantly the results of these pilot studies clearly indicated a suitable column loading capacity had been obtained,

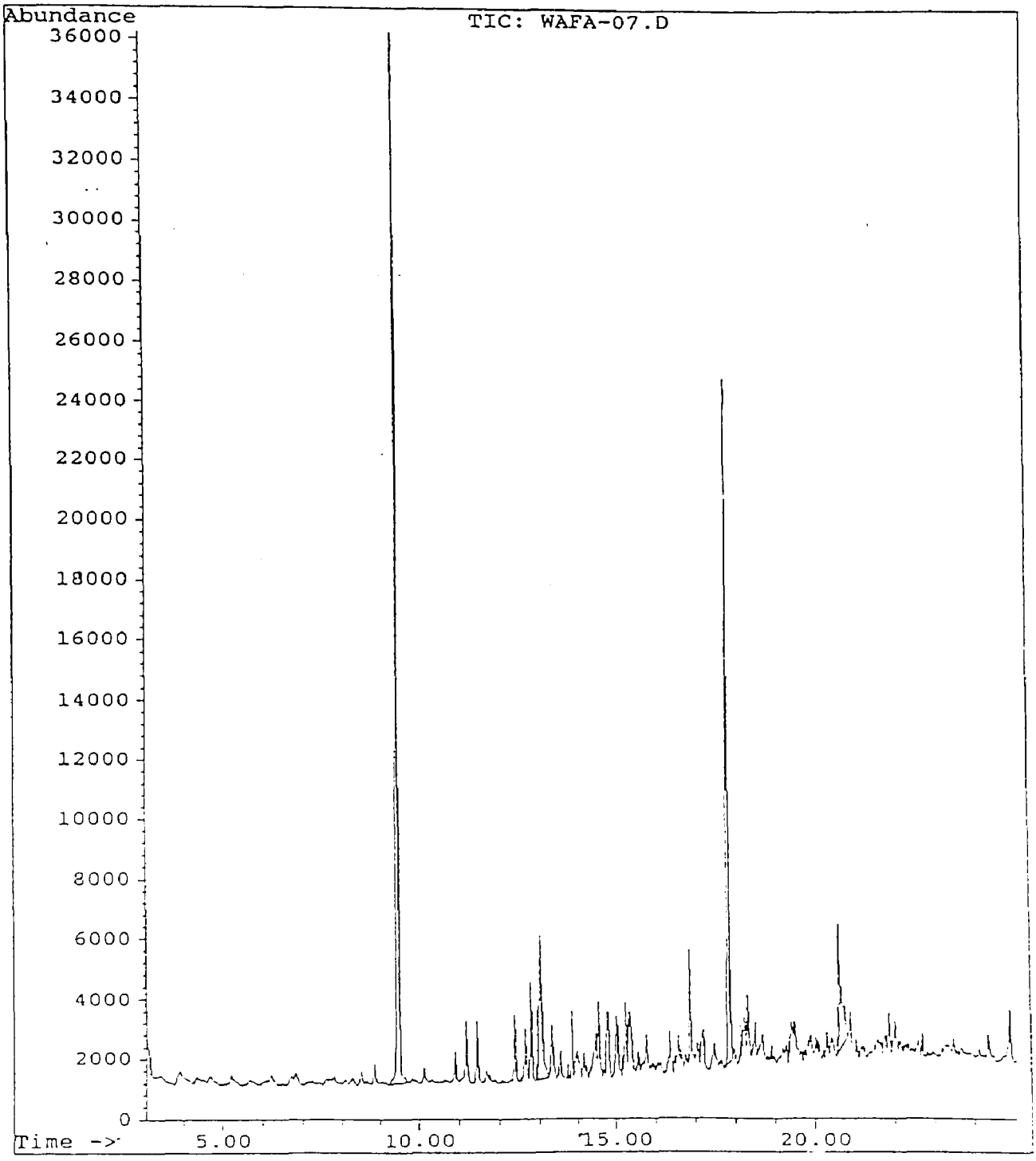
although this could be optimised it was decided to scale-up the column chromatography fractionation procedure immediately to produce a more concentrated aromatic fraction which could be studied by full scan GC/MS.

3.3 Scaled- up fractionation of Libyan crude oil

It was decided to scale-up by a factor of ten such scale-up by procedures have documented[8].

The column used was 60 cm long with an internal diameter of 4 cm. The column was dry packed with 250 g of silica gel from the same batch used in the pilot studies. This resulted in a column of silica whose dimensions were 28 cm long by a diameter of 4 cm. The column was conditioned with 250 cm^3 of hexane. Approximately 10 g of Libyan crude oil were dissolved in 100 cm^3 of hexane and this solution was applied by gravity to the column which was subsequently washed with 500 cm^3 hexane to produce fraction one. Fraction two was produced by washing the column with 500 cm^3 hexane:benzene (75:25). Fraction three was produced by washing the column with 500 cm^3 benzene:methanol (50:50). All three fractions were subjected to full scan GC/MS analysis. Numerous aromatic compounds were identified in fraction two, see figure 4. A full listing of the aromatic compounds identified are given in table 1. Following these analyses it was decided that quantitative studies should be undertaken to estimate the recoveries of aromatic species using the column chromatography method developed.

Figure 3. GC/MS analysis of fraction one of Libyan crude oil obtained by column chromatography. Column specification given in section 3.2. GC/MS conditions given in appendix.



3.4 Estimation of the recoveries of aromatic compounds by column chromatography fractionation.

Polyaromatic hydrocarbons were selected as target analytes for this investigation. A 1 g sample of Libyan crude oil was spiked with seven PAHs at a high level. The level that was selected meant that any contribution to individual PAH recoveries from these species being naturally present within the sample would be negligible. Some initial experiments were conducted to determine the ion counts of endogenous PAHs in the Libyan crude oil against a solution for high level spiking. The spiking solution was also used to prepare three standard solutions with the pesticide o,p-dichloro biphenyl dichloro-ethene (DDE) as internal standard. This pesticide was selected since it could be well resolved from the target analytes and gave an intense molecular ion at m/z 318 under EI conditions. The 1 g of spiked crude oil was applied and fractionated under identical conditions to those previously specified in section 3.2. All three fractions thus obtained were evaporated to dryness under a stream of nitrogen and made up to 50 cm^3 with DDE acting as internal standard. A series of calibration graphs were constructed in full scan mode and examples are shown in figures 5-6. Following the construction of these graphs the recoveries of the individual PAHs were calculated and it was found that only fraction two contained the target PAHs to any great extent. The calculated recoveries of the PAHs are shown in table 2.

Figure 4 GC/MS analysis of fraction two of libyan crude oil, column chromatography.

Column specifications given in section 3.3 GC/MS conditions given in appendix

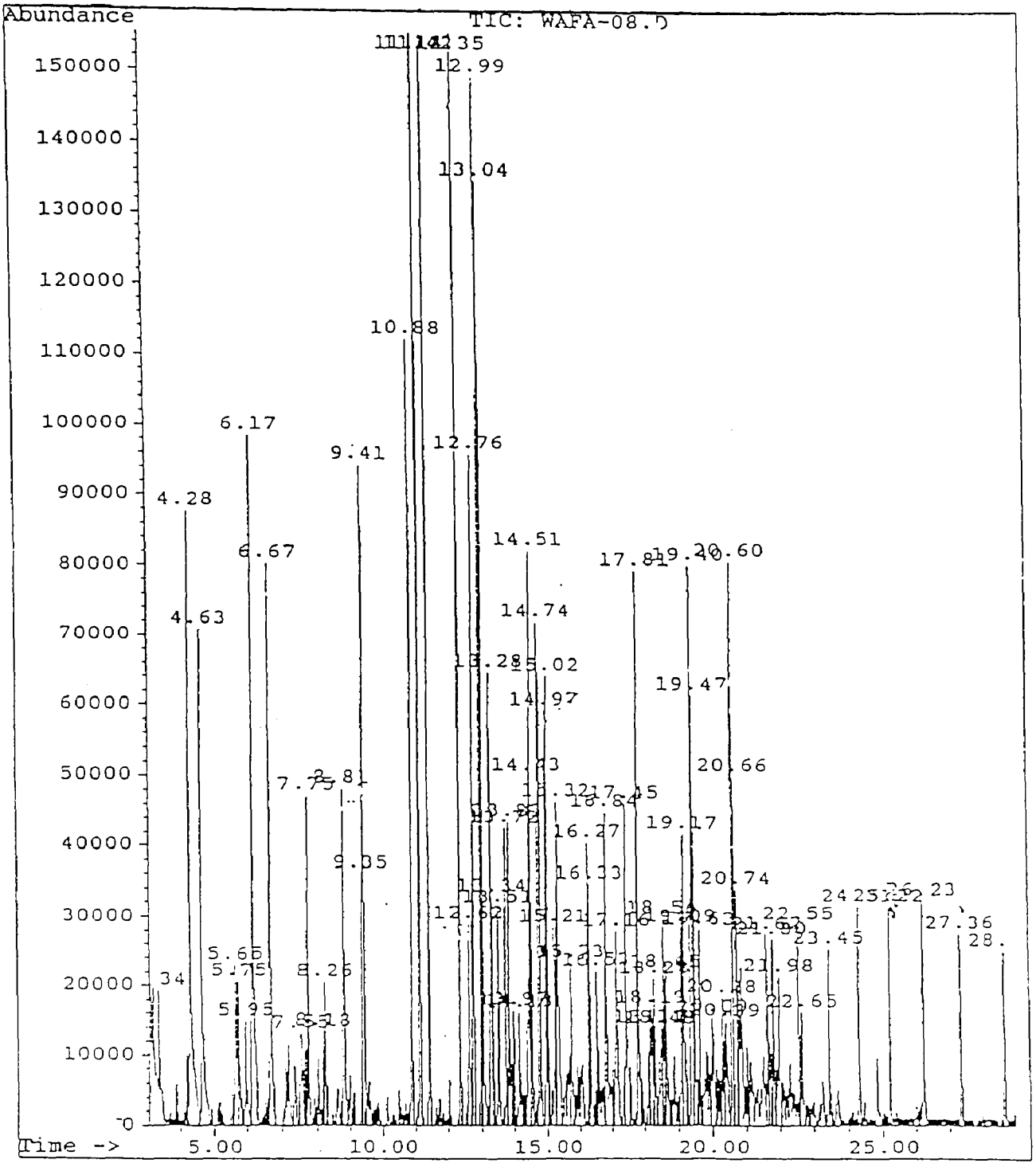


Table 1. GC/MS Library search results obtained from the Chromatogram shown in figure 4. Only Aromatic Compounds are Tabulated.

Peak No	Retention time/min	Compounds name	% Certainty
1	4.28	1,4-dimethylbenzene	95
2	4.63	1,3-dimethylbenzene	87
3	5.65	1-ethyl-4methylbenzene	90
4	5.95	1-ethyl-4methylbenzene	83
5	6.17	1,2,3-trimethylbenzene	90
6	6.66	1,2,3-trimethylbenzene	91
7	7.55	2-ethyl-1,2-dimethylbenzene	90
8	8.18	4-ethyl-1,2-dimethylbenzene	83
9	8.81	1,2,3,4-tetramethylbenzene	90
10	9.41	Naphthalene	94
11	11.14	1-methylnaphthalene	91
12	11.42	1-methylnaphthalene	91
13	12.35	2-ethenylnaphthalene	55
14	12.76	2,6-dimethylnaphthalene	97
15	12.99	2,6-dimethylnaphthalene	97
16	13.04	1,6-dimethylnaphthalene	98
17	13.28	1,4-dimethylnaphthalene	96
18	13.34	1,7-dimethylnaphthalene	94
19	13.51	1,2-dimethylnaphthalene	90
20	13.97	2,4a-dihydro-Fluorene	37
21	14.13	1-methylethylnaphthalene	86
22	14.43	1,4,6-trimethylnaphthalene	96
23	14.51	1,4,6-trimethylnaphthalene	96

24	14.74	1,4,6-trimethylnaphthalene	95
25	14.97	1,4,6-trimethylnaphthalene	96
26	15.02	2,3,6-trimethylnaphthalene	76
27	15.32	1,4,6-trimethylnaphthalene	90
28	16.33	1-methyl-7-(1-methyl)napht	80
29	16.53	2-chloro-1-ethyl-5-methox.B	64
30	16.84	1-methyl-9H-Fluorene	76
31	17.16	1-methyl-7-(1-methyl)napht.	58
32	17.81	Anthracene	90
33	18.11	2,3-dimethyl-9H-Fluorene	74
34	18.19	2,3-dimethyl-9H-Fluorene	72
35	18.28	2,3-dimethyl-9H-Fluorene	91
36	18.48	Phenanthrene,9,10-di-1-met.	32
37	18.65	Methyldibenzothiophene	43
38	19.09	9-methylphenanthrene	80
39	19.17	9-ethyline-9H-Fluorene	59
40	19.40	9-methylphenanthrene	74
41	19.47	2-methylanthracene	74
42	20.00	1,1-(3-methyl-1-prop)-Benz.	37
43	20.28	Benzenamine,4-methoxy-N	12
44	20.39	Naphthalene,1,2-dihydro-4-	47
45	20.60	2,5-dimethylphenanthrene	97
46	20.66	2,5-dimethulphenanthrene	90
47	20.74	2,7-dimethylphenanthrene	96
48	21.80	2,3,5-trimethylphenanthene	87
49	21.98	2,3,5-trimethylphenanthene	72

Figure 5- Calibration graph for quantification of Phenanthrene

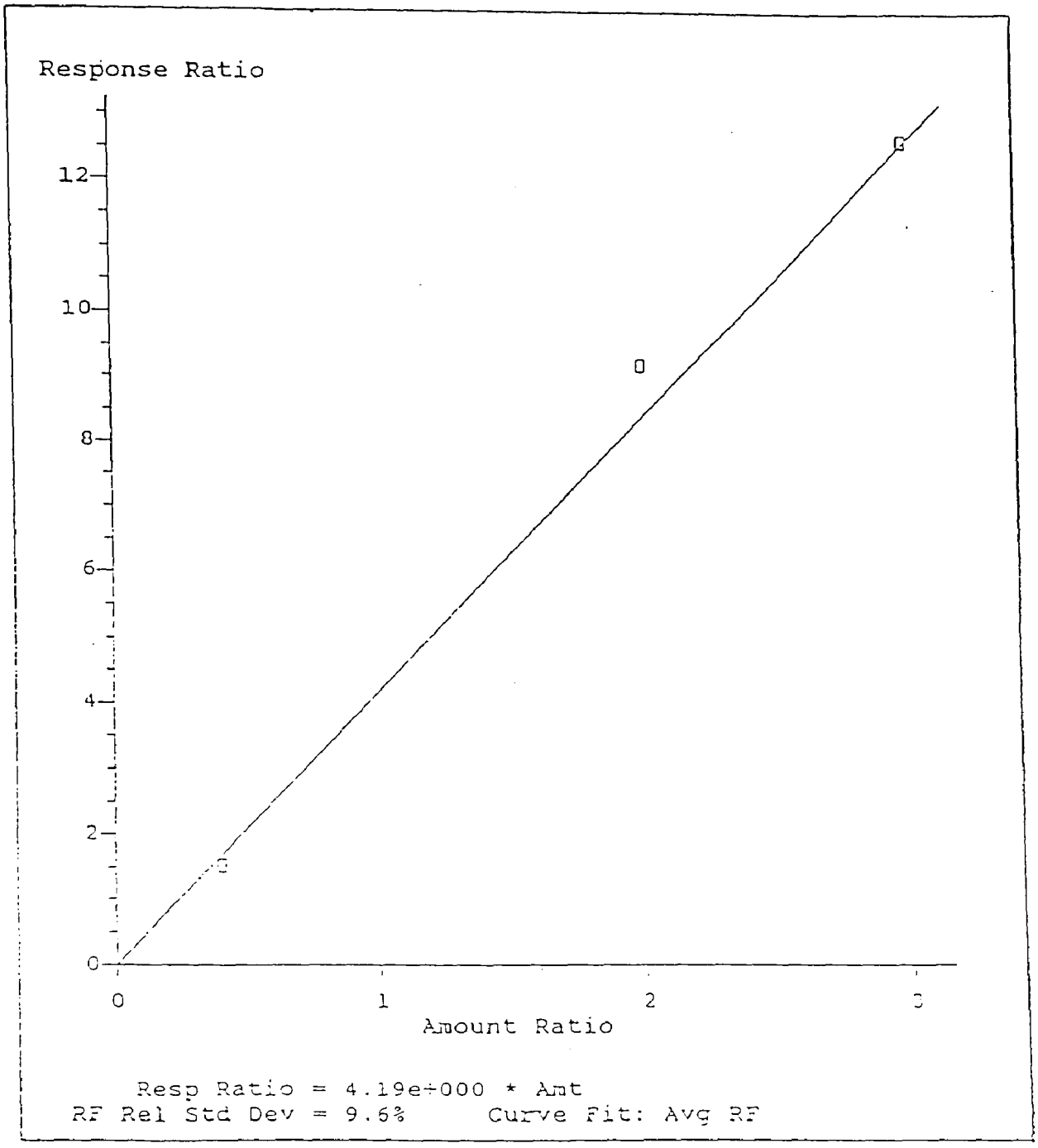


Figure 6. Calibration graph for quantification of Anthracene

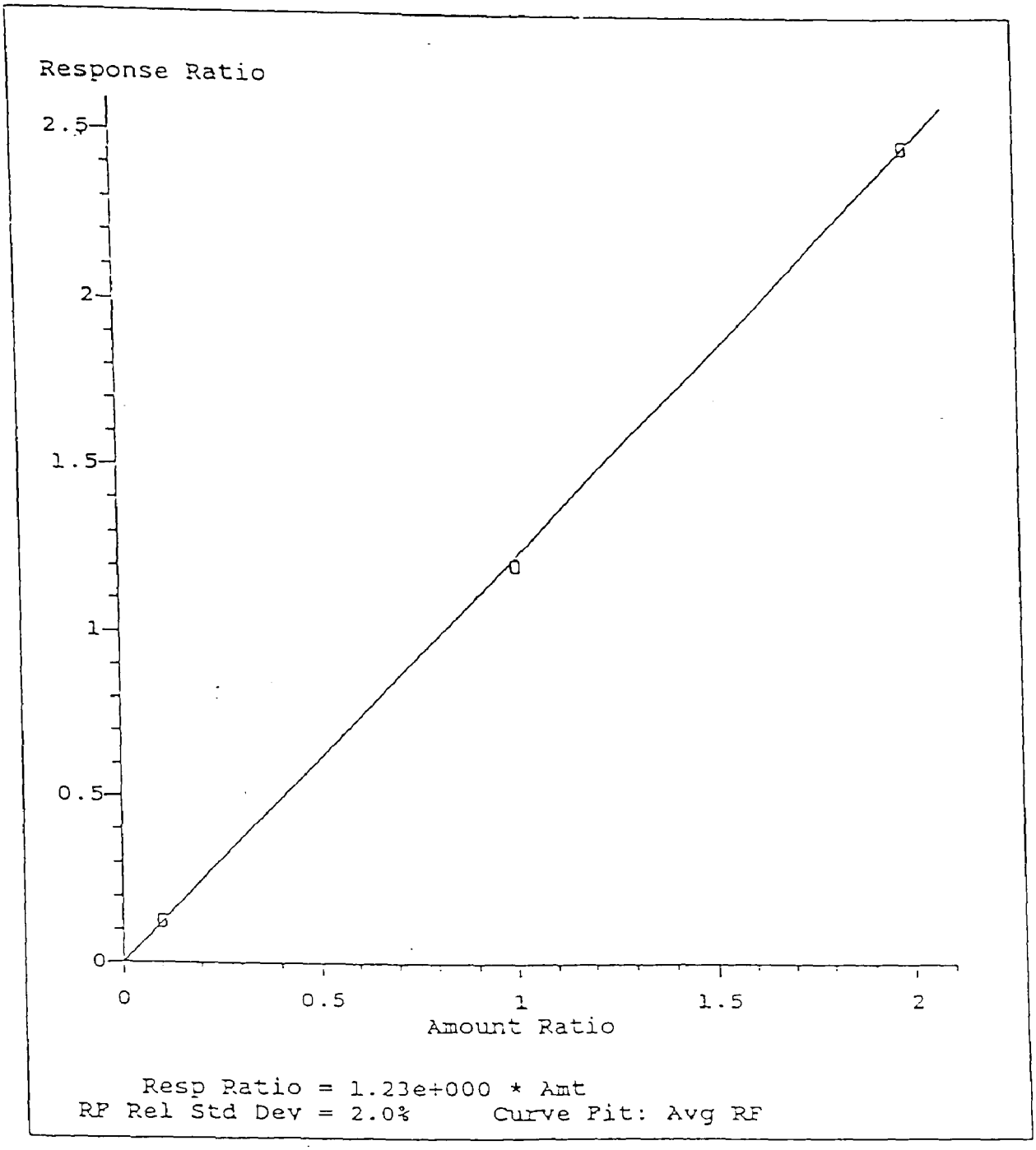


Table 2 Calculated recoveries of the individual PAHs

in column chromatography fraction two.

Peak	Compound	Retention time	Calculated $\%^{w/w}$ recoveries
1	Naphthalene	9.42	94
2	Fluorene	15.30	95
3	Phenanthrene	17.83	96
4	Anthracene	17.83	96
5	Fluoranthene	21.02	96
6	Pyrene	21.58	46
7	DDE (int.std)	21.93	....
8	Chrysene	24.87	98

3.5 *Discussion*

Column chromatography provides a rapid and simple means for the fractionation of crude oils. With the higher sample loading capacity to that possible with SPE cartridges it was possible to determine the aromatic profile of Libyan crude oil. PAHs were selected as target analytes to estimate the recoveries of aromatic species by column chromatography and in all instances these were recovered at high levels. If recoveries of other endogenous aromatic species in Libyan crude oil were required then appropriate standards could be purchased. The use of isotopically labelled internal standards would remove the necessity for spiking at a high level when percentage recoveries were estimated from PAH spiked crude oil. It seems likely that individual crude oils could be characterised using this approach to obtain the aromatic profile.

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CHAPTER 4

The use of Supercritical Fluid Extraction for the Fractionation of Crude Oils.

4.1 *Introduction to SFE*

Prior to defining the physical and chemical characteristics of supercritical fluids, the history of supercritical fluid extraction will be briefly reviewed. Interestingly analytical scale SFE followed [1] the successful development and implementation of industrial scale SFE technology. Supercritical fluid extraction (SFE) is a technique that employs a supercritical fluid to effect the solvation and separation of solutes from a matrix.

The phenomenon of supercritical fluids was first documented in 1879 by Hannay and Hogarth [2,3] who reported the results of studies whereby supercritical fluids were used as a means of solvating solids which possessed low vapour pressures. Since these initial reports the solvating power of supercritical fluids largely remained unrecognised until the deposition of solutes from compressed gaseous solutions became evident during the early development of the petrochemical industry [4].

The solvating properties of liquefied gases were investigated throughout the 1940's and 1950's with the pioneering studies of Francis [5]. Despite these initial studies spanning a long period of time, it was Zosal in 1965 who described [6] the potential of supercritical fluid as a media for commercial extraction processes. Since then SFE has been developed in the field of chemical engineering and this has led to the construction of several plants specifically designed to decaffeinate coffee and tea along with plants to isolate the volatile constituents of hops and spices[7,8] . On the industrial scale SFE has also been successfully utilized for :

- The deodorization of : vegetable oil, animal fats and brewers yeast [1,9].
- The aroma recovery from spices, hops, tobacco dust, apples and pears[10,11].
-The recovery of oil from: Soya beans, jajoba beans, palm kernels, cotton seeds, coconuts, peanuts, rice and cocoa has been reported together with fractionation of cod liver oil, fatty acid esters, glycerides mixture and lecithin [1,10].

Background information on the historical, theoretical and practice of supercritical fluid extraction is located in several references[1,9,12,13] .

In the early 1980's, studies into SFE as an analytical tool for laboratory scale work had begun to accelerate[13,14] , this was partly due to the simultaneous development of SFE in several technical disciplines as well as the lack of definition as to what really constitutes "analytical SFE" . However there is little doubt that the efforts of Stahl and Schilz in 1976[15] to combine SFE with TLC demonstrated the considerable potential of the technique for analytical studies .

SFE has recently been successfully applied to the extraction of pesticides from soil[16] , food materials and oil[12,17], alkaloids from plants[18], additives from polymers[19], drugs in animal tissue[20], drugs in blood and urine[21], PAHs from sediments and pitch[22] , volatile components from plants and polymers[23] and fatty acids from food[24].

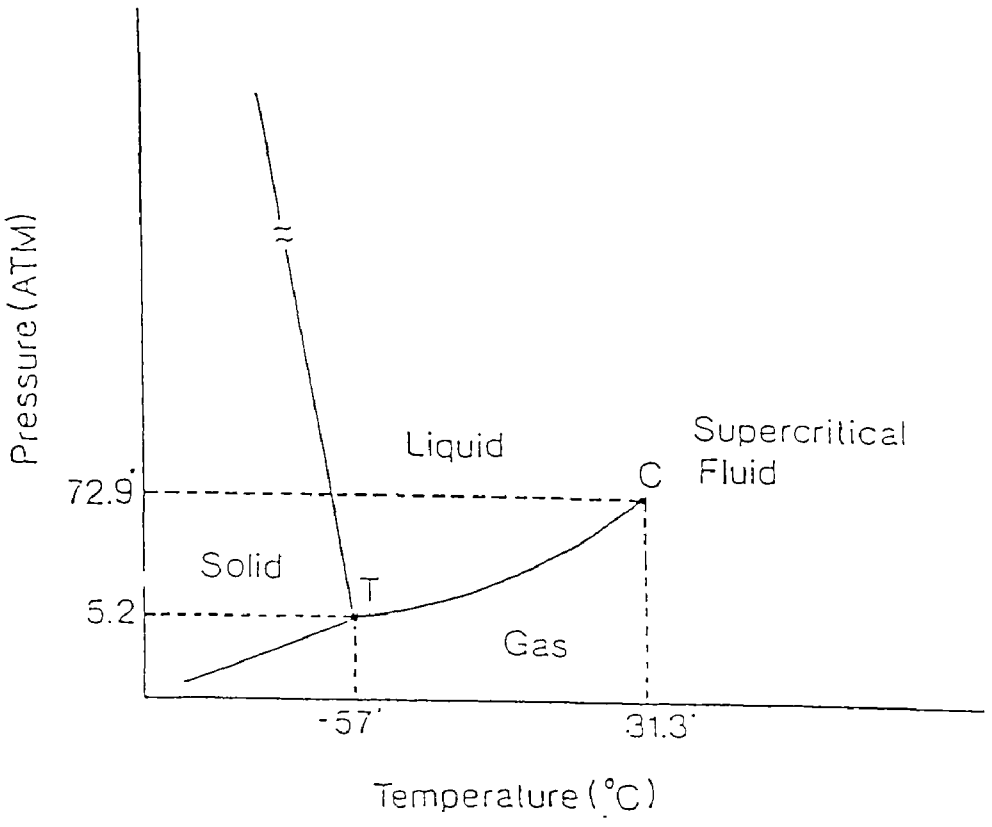
Most commercial scale SFE processes exploit the use of carbon dioxide since it is, relatively inexpensive, non-toxic , non-flammable and whose low supercritical temperature means that it is ideal for the extraction of thermally labile species.

Many of the supercritical fluids described in the following section are either too expensive or hazardous to utilise on the industrial scale and are therefore reserved for analytical applications.

4.2 *Supercritical Fluids.*

A supercritical fluid is a substance that has been elevated above its physical critical points . Figure 1 shows the phase diagram of pure carbon dioxide in which the regions corresponding to solid, liquid and gas phases are indicated. The vapour pressure curve starts at the triple point (TP), and ends at the critical point (CP). The melting pressure curve starts at the triple point and rises steeply with increasing temperature and pressure. The sublimation curve starts at the triple point and goes down slowly with decreasing temperature and pressure. The point at with the liquid and gas phases merge is called the critical point with the pressure and temperatures at this point being denoted as the critical pressure and critical temperature respectively. Below this point two or three of the phases, can co-exist in equilibrium along the vapour pressure, melting, and sublimation lines.

Figure 1 Phase Diagram of CO_2



In the region above the critical point (CP), the substance can not be liquefied by increasing the pressure or gasified by increasing the temperature, there is no phase transition from gas to liquid, or vice versa. The substance in the supercritical region is neither a liquid nor a gas and it is generally referred as a fluid irrespective of density. Table 1 shows a comparison of average values of important physical properties of the three common states. The diffusivity of a supercritical fluid is higher than that of a liquid by a factor of several hundred; this means that mass transfer in a supercritical fluid is faster than in the liquid by the same factor.

TABLE 1

Physical properties of gases, liquids, and supercritical fluids CO_2[24]

properties	units	Gas	Liquid	SF
Density	wt/volume	10^{-3}	1	0.3
Diffusivity	Dm(cm^2/s)	10^{-1}	$5x10^{-6}$	10^{-3}
Viscosity	(g/cm.s)	10^{-4}	10^{-2}	10^{-4}

Inspection of table 1 reveals that the viscosity of supercritical carbon dioxide is one hundred times lower than liquid carbon dioxide but that the densities are similar. The combination of these properties means that a supercritical fluid penetrates a material as though it was a gas, but with the very important difference that it has solvating

properties approaching that of liquid. These gas like transport parameters contribute to improved rates of mass transfer thus resulting in faster extraction than that achievable using traditional solvent extraction techniques.

By far the most widely used extraction fluid is supercritical fluid CO_2. Table 2 shows a selection of compounds and their associated critical properties which have also been used in performing supercritical extraction.

Table 2 Critical Parameters of Selected Fluids[1]

Fluid	(Tc °C)	(Pc atm)	Density(g/cm^3)
CO_2	31.1	72.8	0.468
N_2O	36.4	71.5	0.452
SF_6	45.5	37.0	0.738
SO_2	158	78.0	0.525
CS_2	279	78.0	0.448
H_2O	374.1	217.6	0.322
Methanol	239.4	79.9	0.272
Ethanol	243.0	63.0	0.276
Propanol	263.5	51.0	0.275
Diethyl Ether	193.6	36.3	0.267
Acetonitrile	274.7	47.7	0.237
Ammonia	132.3	111.3	0.235
Ethane	32.4	48.3	0.203
Ethene	10.0	51.2	0.227
Trifluoromethane	25.9	47.7	0.516
Chlorotrifluoromethane	28.8	38.7	0.580
Dichlorodifluoromethane	111.7	39.4	0.557

Many of the listed fluids would not be suitable for practical extraction due to their unfavourable physical properties, cost, or reactivities. For example, ethene which exhibits a subambient critical temperature is of limited value due to its high flammability. Polar fluids such as ammonia are useful in the extraction of highly polar and/or high molecular weight solutes which have limited solubility in CO_2. The use of ammonia as a supercritical fluid is limited due to its high reactivity. Ammonia is very unpleasant to work with, a fume hood or other venting precautions are needed to keep it out of the laboratory atmosphere. Nitrous oxide has been used extensively, it is polar and has reasonable critical values. However, there have been reports of violent explosive reactions[25] between nitrous oxide and oils and fats. Other fluids like fluoroform (HCF_3), are unique in their a ability to solvate basic solutes through intermolecular hydrogen bonding in the supercritical state[25], however, the exorbitant cost of the fluid can limit its use for SFE. The solvent strength of low polarity fluid such as CO_2 can be increased by the addition of polar modifiers.

There are many polar organic solvents such as alcohols, ethers, tetrahydrofuran, and chloroform that can be mixed with CO_2. The use of supercritical fluid modifier mixtures offers the advantage of enhanced solvent properties for rapid separation and controlled selectivity since the modifier and its concentration can be widely varied. Other factors which contribute to the wide popularity of using supercritical carbon dioxide include :

1) The critical temperature of CO_2 (31.1°C) is only slightly above room temperature. Generally low temperatures are desirable to avoid thermal degradation of analyses.
2) The critical pressure of CO_2 (1070 psi) is easy to obtain.
3) Carbon dioxide is non-flammable, odourless, and chemically inert.
4) It is available in good purity at low cost.
5) It does not present a disposal problem.

Supercritical CO_2, by itself, is a low polarity solvent. Even so, its solvent power varies considerably with density. It has been proved [26] that extraction with supercritical CO_2,

can be far superior to conventional methods of extraction (such as liquid extraction, soxhlet, extraction etc.) Compared to conventional methods such as Soxhlet extraction, the speed at which SFE can be done is remarkable, SFE of polycyclic aromatic hydrocarbons from river sediments have been reported [27] to be completed in 30 minutes using a mixture of methanol-nitrous oxide as supercritical fluid, while the same sample took 8 hours with dichloromethane sonication methods and 4 hours using dichloromethane Soxhlet extraction. Typical SFE extraction times reported in the literature are within the order of 30 minutes to 2 hours[28], whilst conventional methods often take more than a day.

One of the most commonly-used extraction methods involves the use of Soxhlet apparatus which first reported by Tswett in 1906 [29]. Samples prepared by Soxhlet extraction are typically analysed via a wide range of chromatographic techniques which in some instances are interfaced to mass spectrometers to enable a high level of confidence in the results. However, in some instances the results of the analysis may not be available for several days. The mass spectrometry analysis can be done quickly enough, but preparing the sample for the analysis to be carried out can take up to 24 hours which severely limits the rate at which incoming samples can be analysed. SFE enables high sample throughput in the analytical laboratory since sample preparation time is often greatly reduced.

Since the extraction of organic compounds from sample matrices is often the most error-prone and slowest stage of an entire analytical scheme, the replacement of liquid solvent extraction with SFE has several potential advantages :-

SFE is fast: Mass transfer is faster in a supercritical fluid than in liquid solvents because supercritical fluids have solute diffusivties an order of magnitude higher (10^{-4} vs 10^{-5} cm^2/s) and viscosities (10^{-4} vs. 10^{-3}. s/m^2) an order of magnitude lower than liquid solvent. In appropriate cases quantitative SFE can be completed between 10 to 60 minutes whereas several hours are required for the sample liquid solvent extraction[30].

Variable solvent strength: The solvent strength of SFE depends on its density[27,31,32] and the solvent strength can easily be manipulated by changing temperature and pressure at which the extraction takes place. Incorporation of organic modifiers to the supercritical fluid media vastly extends the utility of the SFE technique since a high degree of selectivity is possible for the extraction of compounds from mixtures of different compound class.

Reduction of liquid solvent usage: Liquid solvent extraction techniques use relatively large volumes of organic solvents. Recent concern has focused on the potentially toxic and flammable nature of the organic solvents used and their rapidly - increasing disposal costs. SFE largely overcomes these problems especially when extractions are performed using carbon dioxide.

Automation and Hyphenation: Recent commercially available SFE systems under microprocessor control are equipped with carousels and this facilitates the unattended extraction of numerous samples.

There are two basic approaches to analyses which involve the use of SFE i.e. off-line in which the extracts are transferred to the instrumentation which is the final stage of the analysis and on-line in which the SFE system is directly coupled to the instrument to be used for the final analysis. A variety of on line techniques have been reported and these include ; SFE-GC [33,34,35] SFE-HPLC [36] , SFE-SFC [16,37] and even SFE-SFC-MS-MS [38] . Depending upon the SFE approach adopted the extracts can be collected into a few cm^3 of liquid solvent ("off-line" SFE) or the analyses are transferred directly to a chromatographic system ("on-line" SFE).

The majority of SFE studies reported to date have utilised off-line procedures since it is inherently simpler to perform. Table 3 lists the essential features of the off-line and on-line SFE techniques [39].

Table 3 Comparison of off-line and on-line SFE[40]

	off-line	on-line
GC or SFC needed for extraction ?	no	yes
100% transfer of analyses ?	no	yes
multiple injection per extract ?	yes	no
polar modifiers useful ?	yes	??
sample handling between SFE analysis	yes	no
maximum convenient sample size	10-15 g	1-3 g

4.3 Elimination of Concentration Step

Soxhlet extraction procedures generally result in the analytes being dissolved in a relatively large volume of organic solvent, typically 250 cm^3. In order to improve final detection limits the dilute solution of the analytes must be subjected to a concentration step e.g. rotary evaporation. Off-line SFE extracts are typically collected in 1-2 cm^3 of solvent and are in contrast immediately ready for final analysis via GC, GC/MS, SFE, etc.

4.4 Analyte Selectivity

During the development of a successful selective SFE procedure there are four basic parameters which need to be considered :

1. The detectable "threshold pressure".
2. The appropriate conditions for selective extraction of solute.
3. The occurrence of solubility maxima in supercritical systems.
4. The knowledge of the physical properties of solute and matrix.

Gidding[32] defined the "threshold pressure" as the pressure at which the solute partitioned into the supercritical fluid, a concept which is very important to selective extraction. A fractionation range exists between the threshold pressure region for the solute and the point where maximum solubility for the solutes is arrived in the supercritical fluid. A selective extraction can only be possible if an appreciable difference exists in the molecular size, polarities, or volatilities of the target analytes and all other species present within the matrix. Selective extraction can be achieved by varying density, temperature or by varying the modified concentration. Recent findings clearly indicate that selectivity can be further enhanced by loading the matrix when appropriate onto chemically modified sorbent cartridges.

4.5 *Instrumentation*

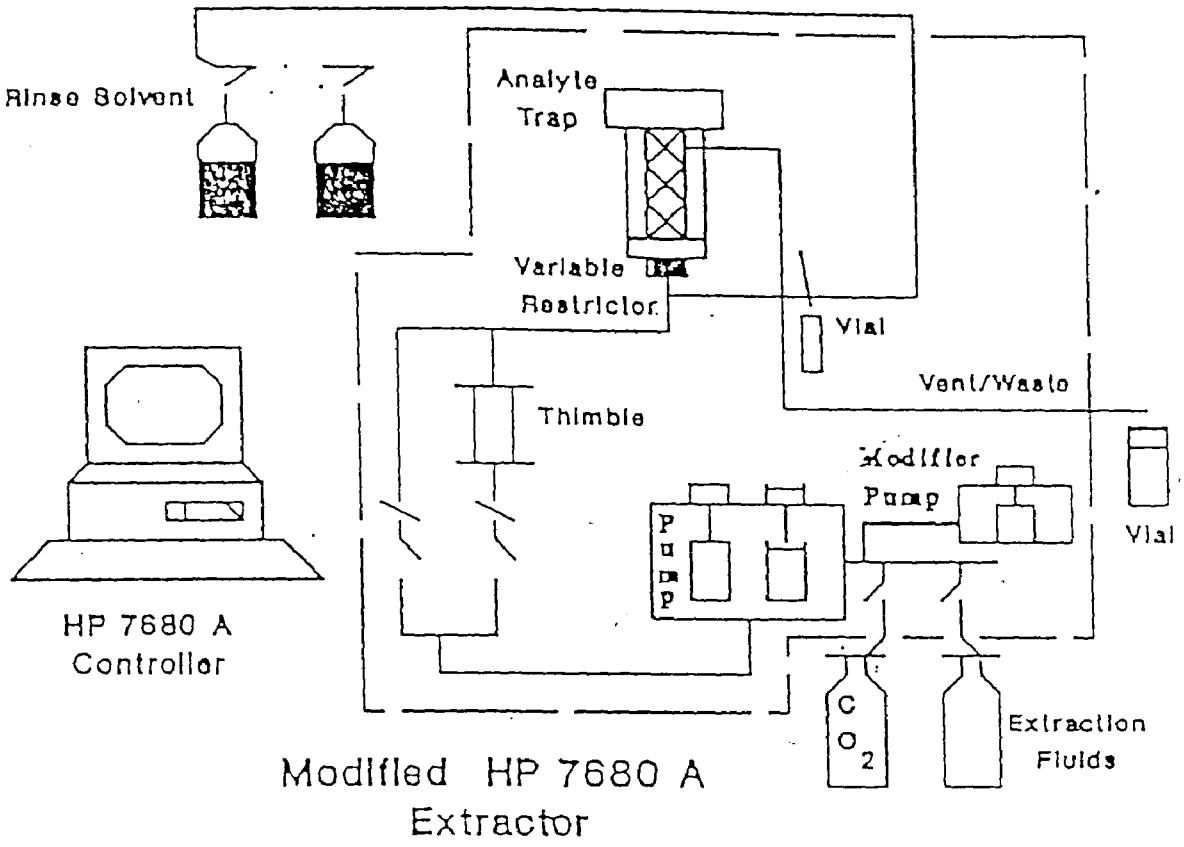
The essential features of a supercritical fluid extractor are as follow : a supply of pure gas (most commonly CO_2), a pump to pressurise the gas to above its critical pressure, an extraction chamber to contain the matrix to be extracted . The extraction chamber is generally housed within an oven whose temperature can be very accurately regulated. A fixed or variable restructure to depressurise the supercritical fluid and an analyte collection arrangement. Pressurisation and liquid supply can be achieved using either syringe or piston type pumps. In order to prime the pump with for example liquid carbon dioxide, a cooling arrangement is generally fitted to the exterior body of the pumping arrangement. Often the extraction chamber is referred to as the thimble whose design enables it to withstand the high pressures which it is subjected to during normal operation. The design of the thimble must incorporate certain features to assure reproducible sample extraction.

Off-line SFE can be performed using either static or dynamic extraction; in the static mode the extraction chamber is pressurised and sealed. In the dynamic SFE mode, the sample within the extraction chamber is continuously subjected to a flow of the supercritical fluid and the dissolved analytes are trapped in a collection vessel. After a set time the cell is depressurised and the extracted material is generally discarded.

A combination of both static and dynamic extraction can also be utilised. Once the analytes have left the extraction vessel, they are separated from the extraction medium by depressurisation. At the point of depressurisation the supercritical fluid medium enters the gas phase and can be vented to exhaust. Restriction is generally achieved via a fixed made from fused silica or metal tubing or by a microprocessor controlled micrometering valve. A variety of methods can be used to collect the extracted analytes at the point of decompression , these include : depressurisation of the SFE extract into a small volume of solvent[40], thermal trapping in a collection vessel[41] , and collection of the analyte on to a packed trap followed by a secondary extraction with a selective solvent[42]. The flow and the volume of the gas after depressurisation is very important for the successful implemtation of the trapping method. High gas flow rates have been found to be responsible for aerosol formation which can result in more than a 90% loss of analyte at the trapping stage [43,44].

When developing an SFE method, several factors must be considered including : flow, temperature, density and supercritical fluid composition . All of these variables must be precisely controlled. Density is an important parameter since it is directly proportional to the solvating power of the fluid. Higher solvating power is associated with higher density. Temperature control is also important since it directly influences the density and thus analyte solubility. Flow is also an important parameter because it can effectively disrupt the partitioning of the analyte between the supercritical fluid and the matrix. All of these parameters directly influence the reproducibility and recovery of extraction and should be independently and precisely controlled in order to provide a robust routine method. Our studies were conducted using a Hewlett Packard SFE Model 7680A . A schematic diagram of the unit is shown in figure 2.

Figure 2. MODIFIED HP 7680A EXTRACTOR.



A weighed amount of sample is placed into the stainless steel extraction thimble, which utilises finger tight fittings. The chosen extraction fluid is delivered by a cooled dual-piston reciprocating pump to a set of high pressure stream selector valves. The fluid then passes through a heating coil where it is heated to a preselected set point at or above the supercritical temperature of the fluid employed. This heating arrangement is situated at the entrance to the extraction chamber. The supercritical fluid is then introduced into the cell containing the sample matrix such that either static or dynamic extraction commences. The solvent stream containing the desolved analytes is then expanded to near atmospheric pressure via the variable restrictor into a nozzle/trap assembly. The nozzle allows instant depressurisation of the supercritical fluid, with concomitant decoupling of flow from pressure; thus the density can be set independently of the flow of the extraction fluid. The analyte is deposited onto a cryogenically cooled trap and CO_2 dissipates to atmosphere. The temperature of the nozzle and trap is controlled independently facilitating maximum recoveries. The "rinse solvent" pump purges a selected solvent through the trap to elute trapped analyte into vials mounted on an autosampler . A wash and rinse cycle controls the volume of solvent supplied to each of the vials. The sample is then ready for analysis by GC/MS and/or any other analytical technique.

4.6 *Preparation of Crude Oil Sample for SFE*

A 1.0 g quantity of crude oil sample was accurately weighed and dissolved in 100 cm^3 of chloroform in a 250 cm^3 round-bottom flask. Approximately 30 g of silica gel (60-120 mesh, BDH, England) were added to the oil solution i.e. a 1:30 ratio. The silica was then solvent stripped via vacuum rotary evaporation with the water bath held at 80 °C. Finally the sample was placed in a vacuum oven for two hours until a constant weight was obtained. The sample was then forwarded for SFE fractionation.

The SFE system and trap washing system as previously described in section 4.5 were carefully primed. The extraction thimble cell and sintered thimble end caps were carefully cleaned with chloroform and then blown dryness via a stream of nitrogen. In a typical experiment the mass of the clean dry thimble and end caps was recorded as 66.1684g. Crude oil sample loaded onto silica gel as previously described was then added to the extraction thimble and the thimble was sealed with the end caps. The mass of the loaded thimble was determined as 71.5440 g. A stainless steel trap was selected and the trap wash solvents were hexane and dichloromethane respectively.

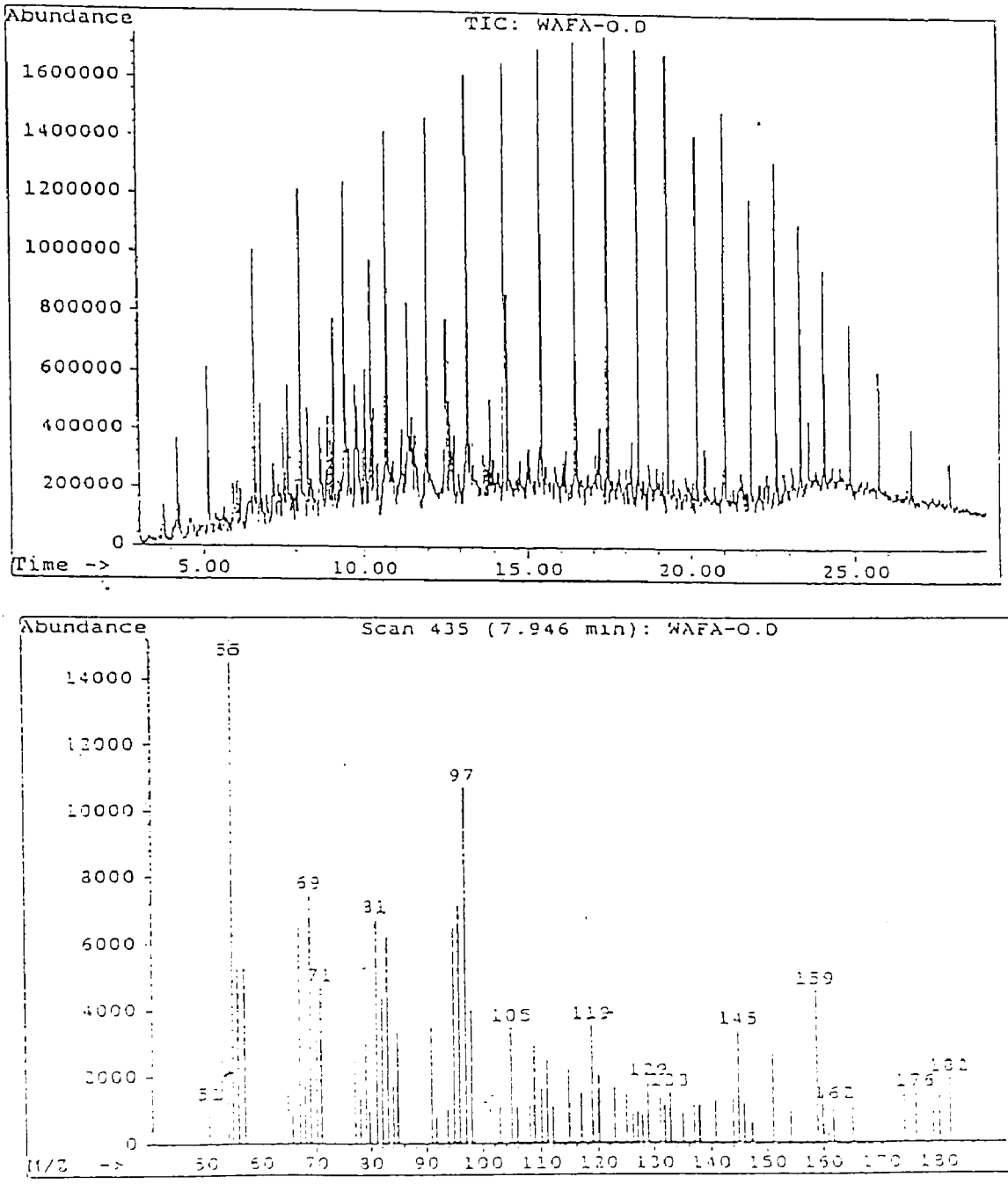
4.7 *SFE Procedure for the Fractionation of Crude Oil*

The conditions used for the extraction of crude oils were as follow :
An extraction chamber temperature of 60 °C was selected and a carbon dioxide fluid density 0.70 g/cm^3 was used for extraction. Each crude oil sample was dynamically extracted for ten minutes onto a trap containing steel particles. The trap was washed to provide three fractions. The first fraction was collected by washing the trap with 2 cm^3 normal hexane and the second and third fractions were collected after sequentially washing the trap with two 2 cm^3 aliquots of dichloromethane. Each fraction was then analysed by full scan GC/MS. The extracted crude oil sample contained within the sealed extraction thimble was then reweighed and was recorded as 71.3313 g i.e. 0.2127 g of the original 1g of crude oil had been extracted.

4.8 *Results and Discussion*

Details of the GC/MS method files used for the analysis of the three crude oil samples isolated via the above SFE procedure are given in the Appendix. The qualitative GC/MS chromatogram for the hexane fraction is shown in figure 3. Equal retention spacing of the peaks is characteristic of a homologous hydrocarbon series. Several of the mass spectra and library search results are shown in figures 4-6. Examination of these spectra reveal that no hydrocarbon molecular ion species were obtained and that this was expected once the EI library matches are examined.

Figure 3. GC/MS analysis of SFE extract obtained by washing the stainless steel trap with hexane. GC/MS conditions given in the appendix.



(a) Chromatogram obtained by GC/MS analysis of hexane fraction. Column J&W Scientific cat. No. 122.5032 30M X O.25mm I.D. Phase DB5 Film Thickness: 25 micron. Method Wafa.O.D. (see apendix).

(b) Mass spectrum obtained for compound whose retention time is 7.946 min.

F igure 4. Mass spectrum obtained for compound whose retention time was 5.119 minutes, shown in fig (a). Library search result shown in fig (b).

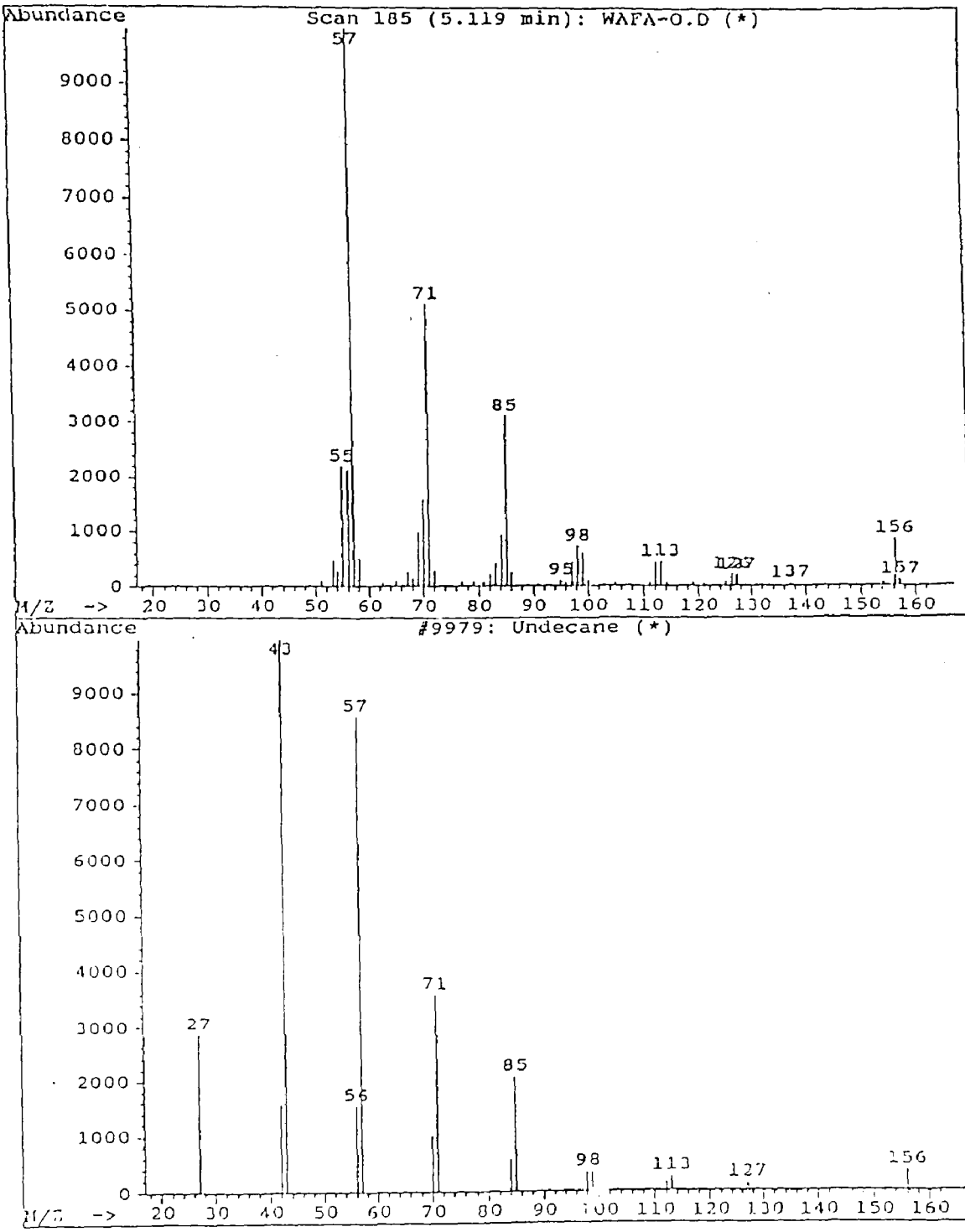


Figure 5. Mass spectrum obtained for compound whose retention timewas 6.576 minutes, shown in fig (a). Library search result shown in fig (b).

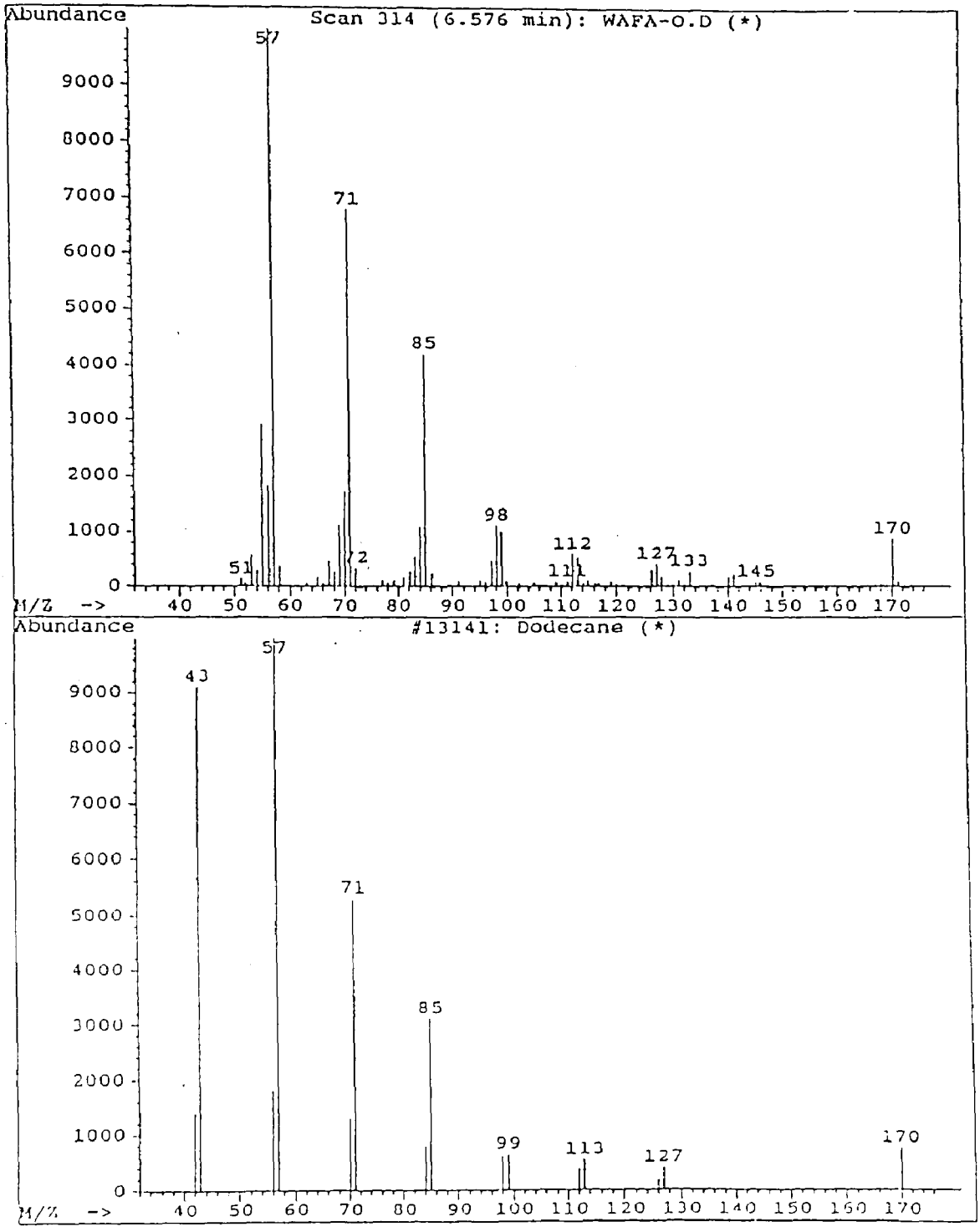
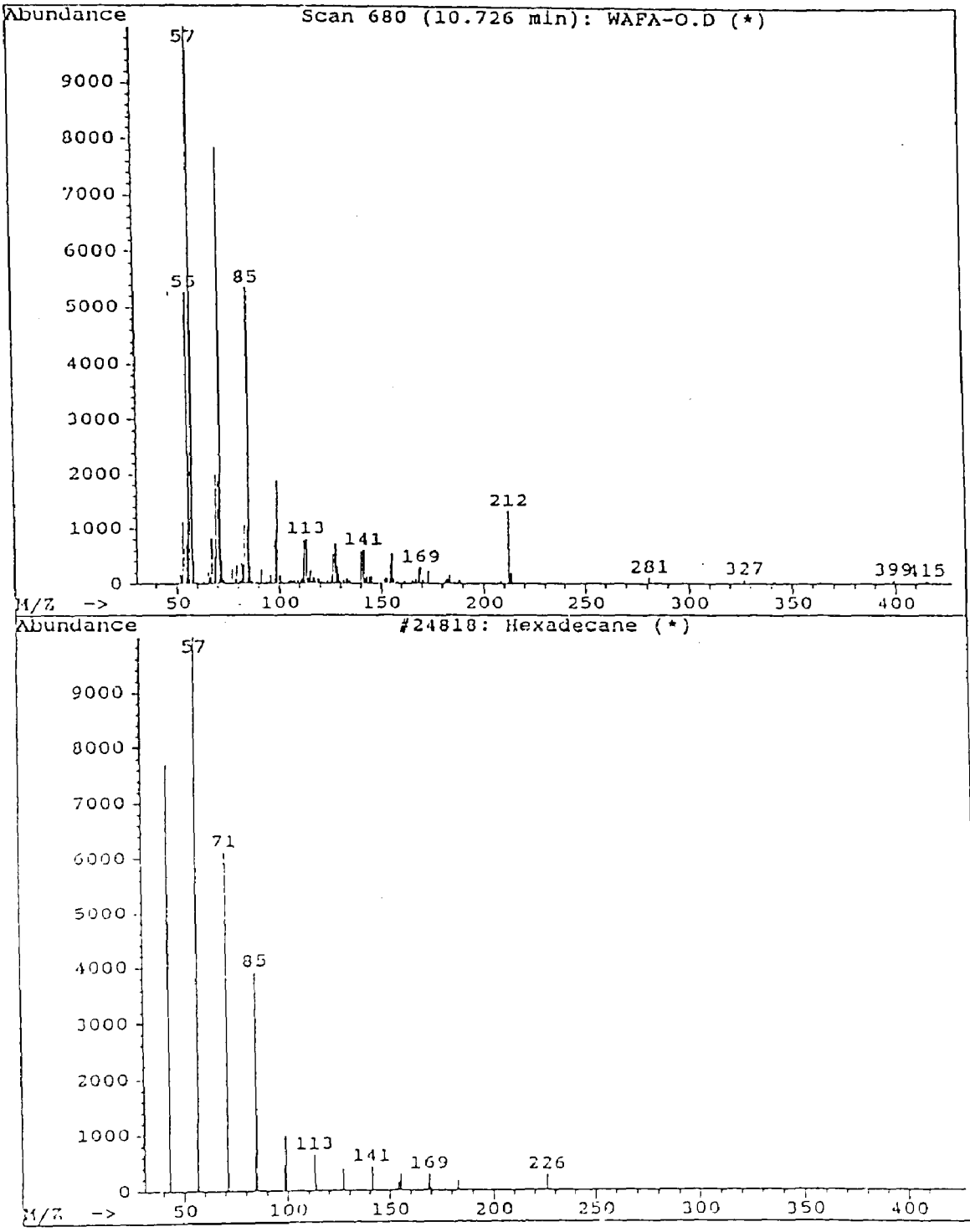


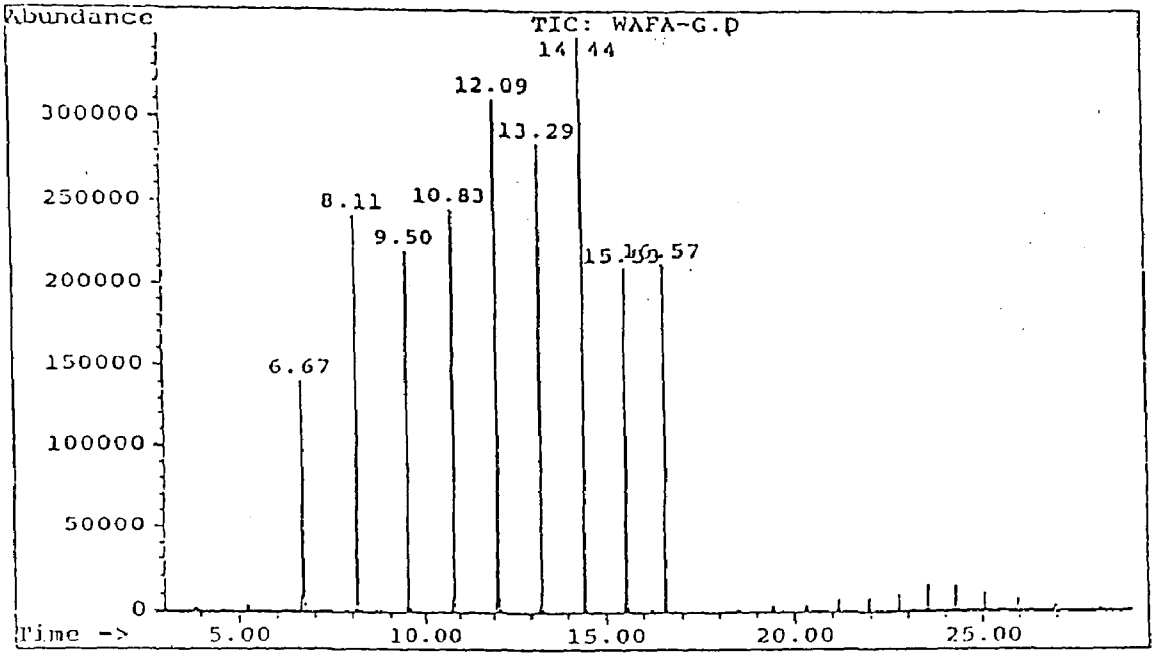
Figure 6. Mass spectrum obtained for compound whose retention time was 10.726 minutes shown in fig (a). Library search result shown in fig (b).



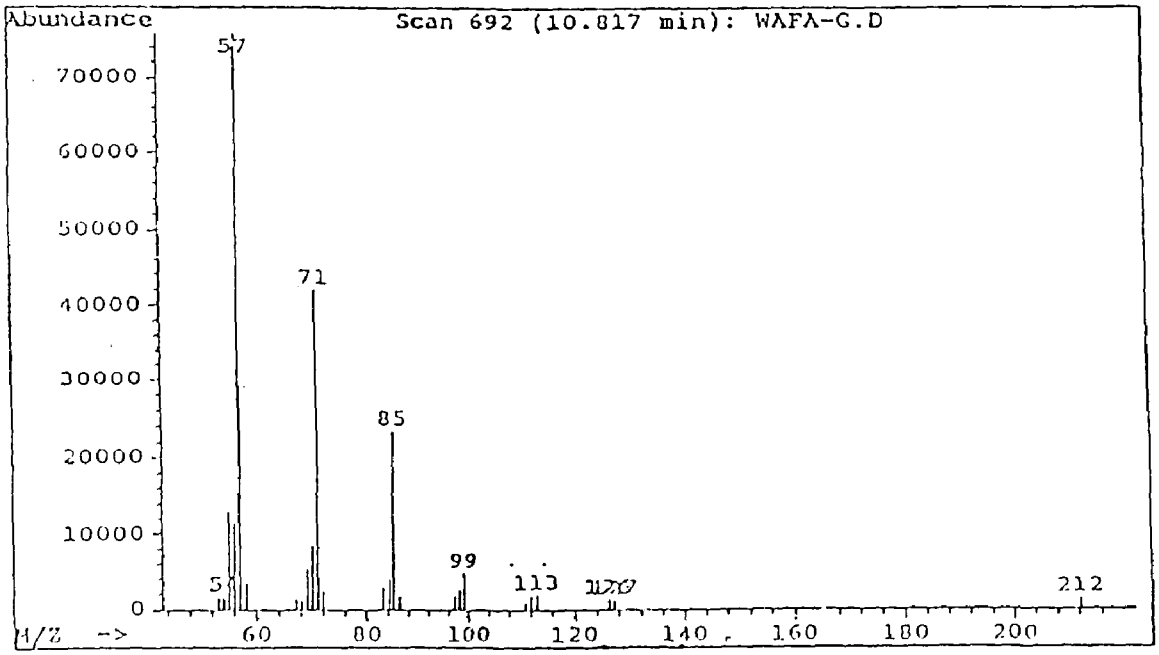
In view of these findings further GC/MS experiments were performed whose objectives were to calibrate the retention times of the unknown hydrocarbons against their respective carbon numbers. This was facilitated via the preparation of a hydrocarbon test mixture composed of nine straight chain hydrocarbons ranging from C-12 to C-20. This mixture was then analysed by the appropriate GC/MS method and typical results of this analysis are shown in figure 7. Each of the nine standard peaks were library searched and typical results are shown in figures 8 - 10. Examination of these results further confirms that molecular ion species are not generally observed for straight chain hydrocarbons when analysed via electron impact ionisation and that the high similarity of the EI mass spectra obtained for the isomers of a hydrocarbon will preclude precise identification. The results of the GC/MS analysis of the standard hydrocarbon retention time calibration mixture are shown in table 4.

With this approach, prior to the analysis of any unknown hydrocarbon samples, the test mixture was also analysed and this procedure proved effective in compensating for any variation of retention time typically caused by varying gas chromatographic performance. In this manner it was determined that the hydrocarbons isolated in the hexane SFE extract varied in carbon number from C-11 to C-34. Ion chromatography , see figure 3, did not indicate the presence of any aromatic hydrocarbons in the test mixture. These initial studies although unsuccessful in providing on SFE procedure for determining the aromatic profile of crude oil did serve to demonstrate the high degree of automation and control of SFE extraction parameters. Future studies would include the incorporation of organic modifiers to the SFE medium in the hope that the aromatic compounds of crude oil could be isolated.

Figure 7. (a) Chromatogram obtained for the GC/MS analysis of a standard hydrocarbon mix ranging from C-12 to C-20. Column conditions as given in fig 3. (b) Mass spectrum obtained for compound whose retention time was 10.817 minutes .

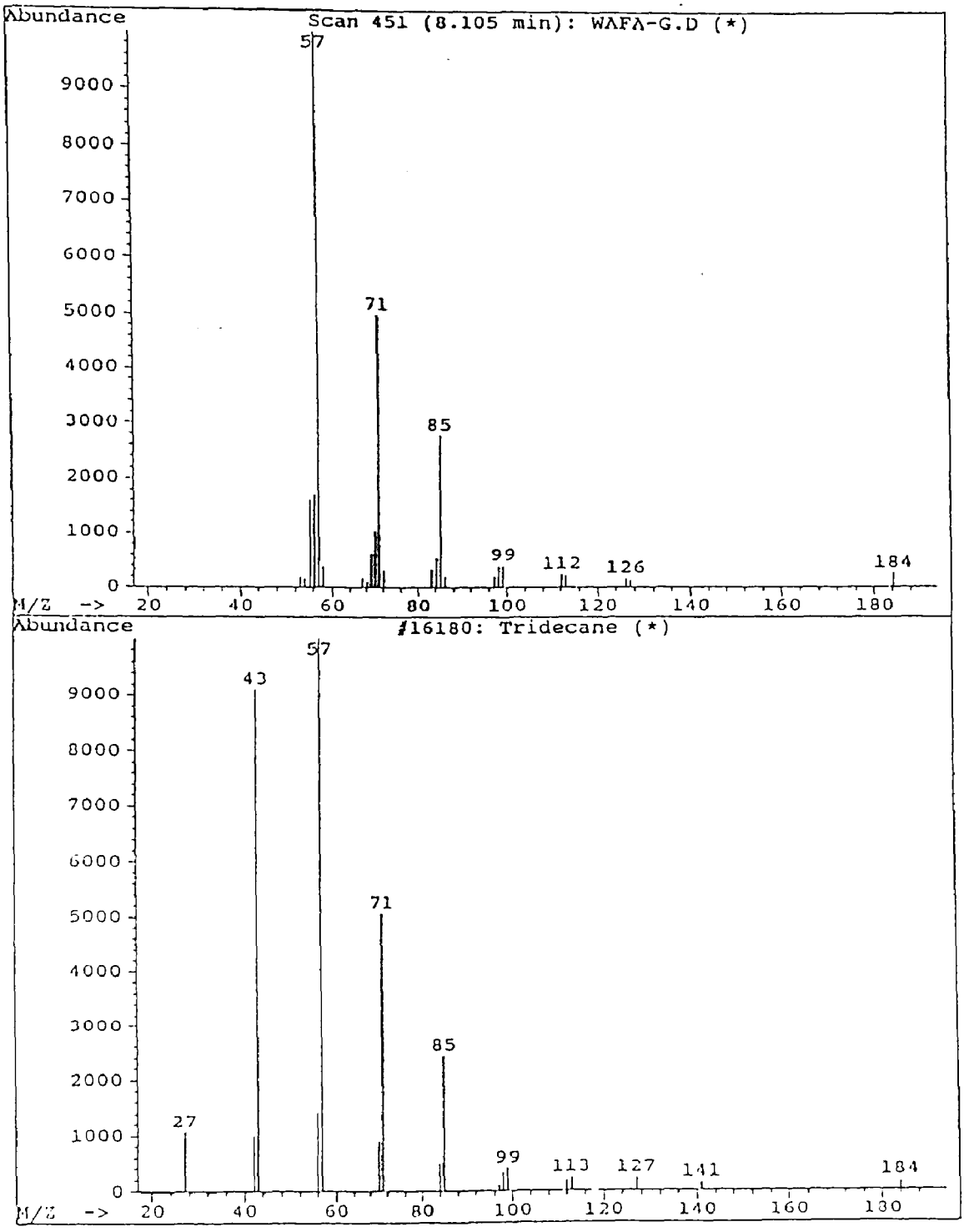


(a)



(b)

figure 8. (a) Mass spectrum obtained for compound whose retention time was 8.105 minutes. Analysis conditions give in fig 3. (b) Library search result.



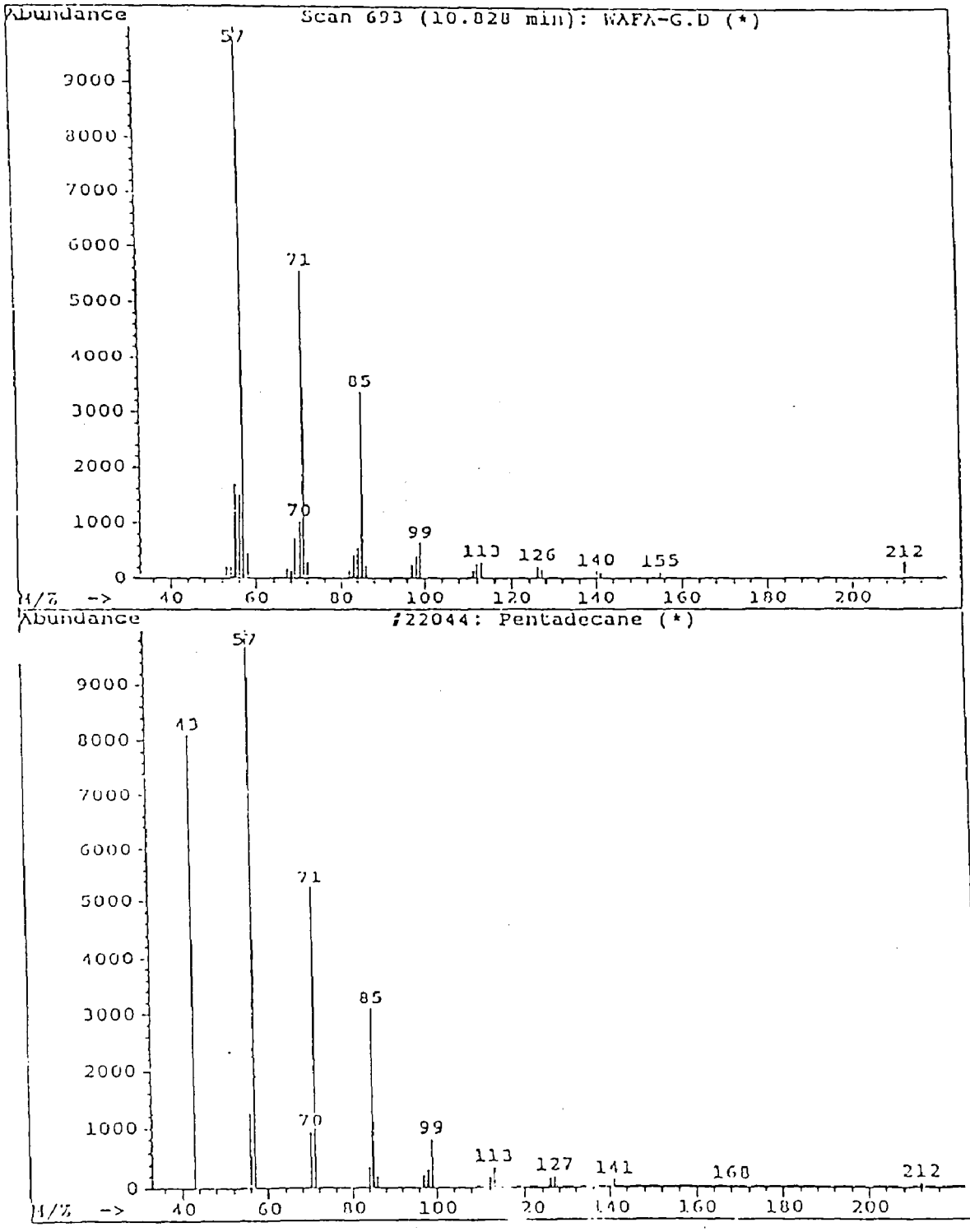
(a)

(b)

(b)

Figure 9. Mass spectrum obtained for compound whose retention time was 10.828 minutes. Analysis condition as given in fig 3.

(b) Library search result shown in fig (b).



(a)

(b)

Figure 10. Mass spectrum obtained for compound whose retention time was 12.088 minutes. Analysis conditions given in fig 3.

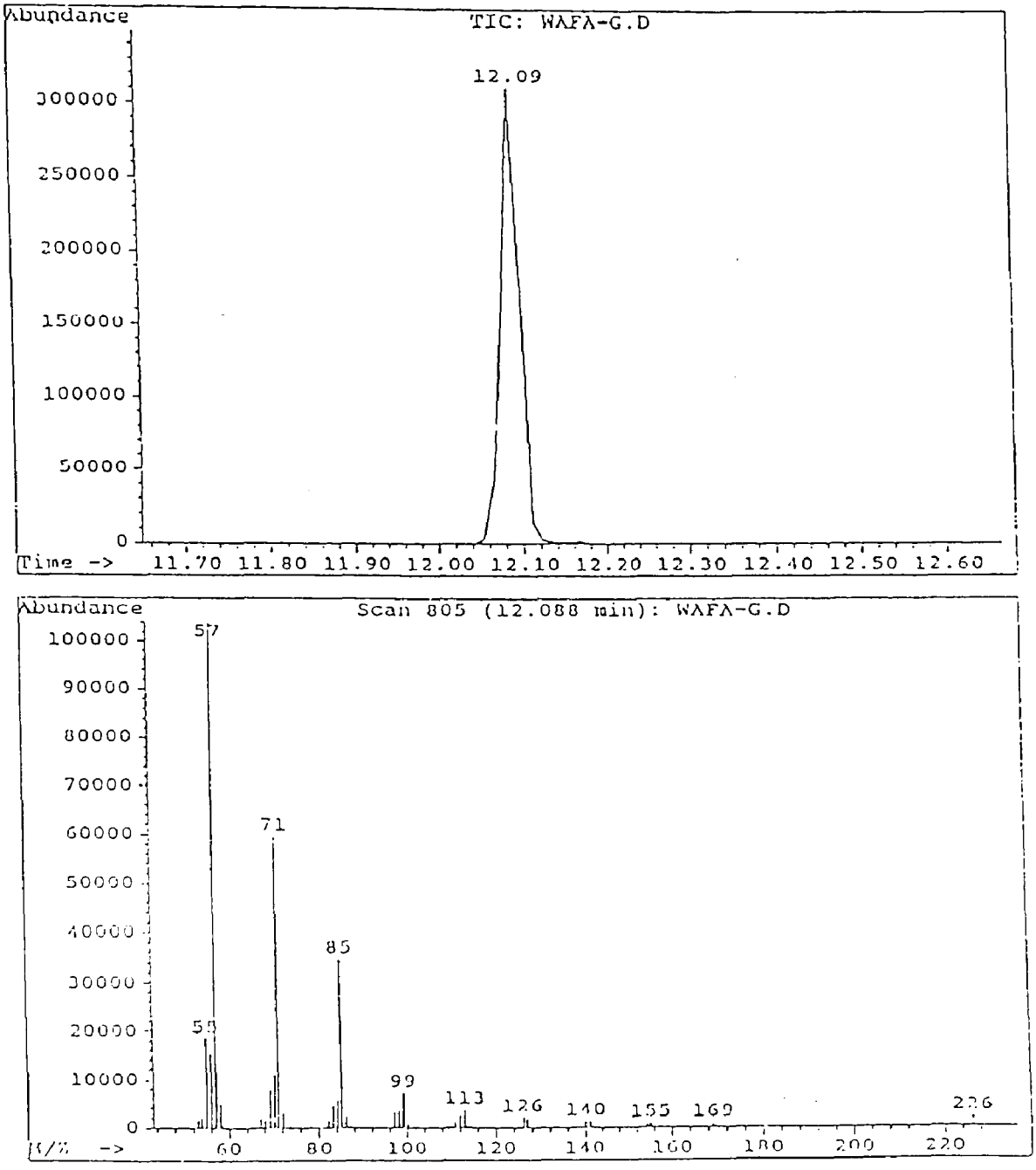


Table 4 Library search results obtained for series of standard hydrocarbons.

Peak	Retention Time	M_r	Actual Carbon No.	Lib.search Result	%Confidence
1	6.67	170	C12	Dodecane	95
2	8.11	184	C13	Tridecane	91
3	9.50	198	C14	Pentadecane	85
4	10.83	212	C15	Tridecane	90
5	12.09	226	C16	Tridecane	86
6	13.29	240	C17	Pentadecane	90
7	14.44	254	C18	Heptadecane	72
8	15.53	268	C19	Heptadecane	91
9	16.57	282	C20	Nonacosane	86

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Chapter 5

Studies Undertaken to Characterise Impurities Associated with the Production of Petrochemical Products

5.1 *Introduction*

The term petroleum is usually restricted to the liquid deposits of crude oil, the gaseous component being known as natural gas and the solid components as bitumen or asphalt. Natural gas may be found associated with crude oil as a gas-cap above the oil or in isolation from oil[1].

Crude oil and natural gas are the raw materials of the petroleum industry. It is the business of the industry to find them, to retrieve them from the earth, to manufacture useful products from them and to sell the products in the markets of the world.

The raw material base for the petrochemical industry primarily depends upon the types of intermediates and final products required by industry and the consumer.

Most petrochemicals are derived from three sources[2]:

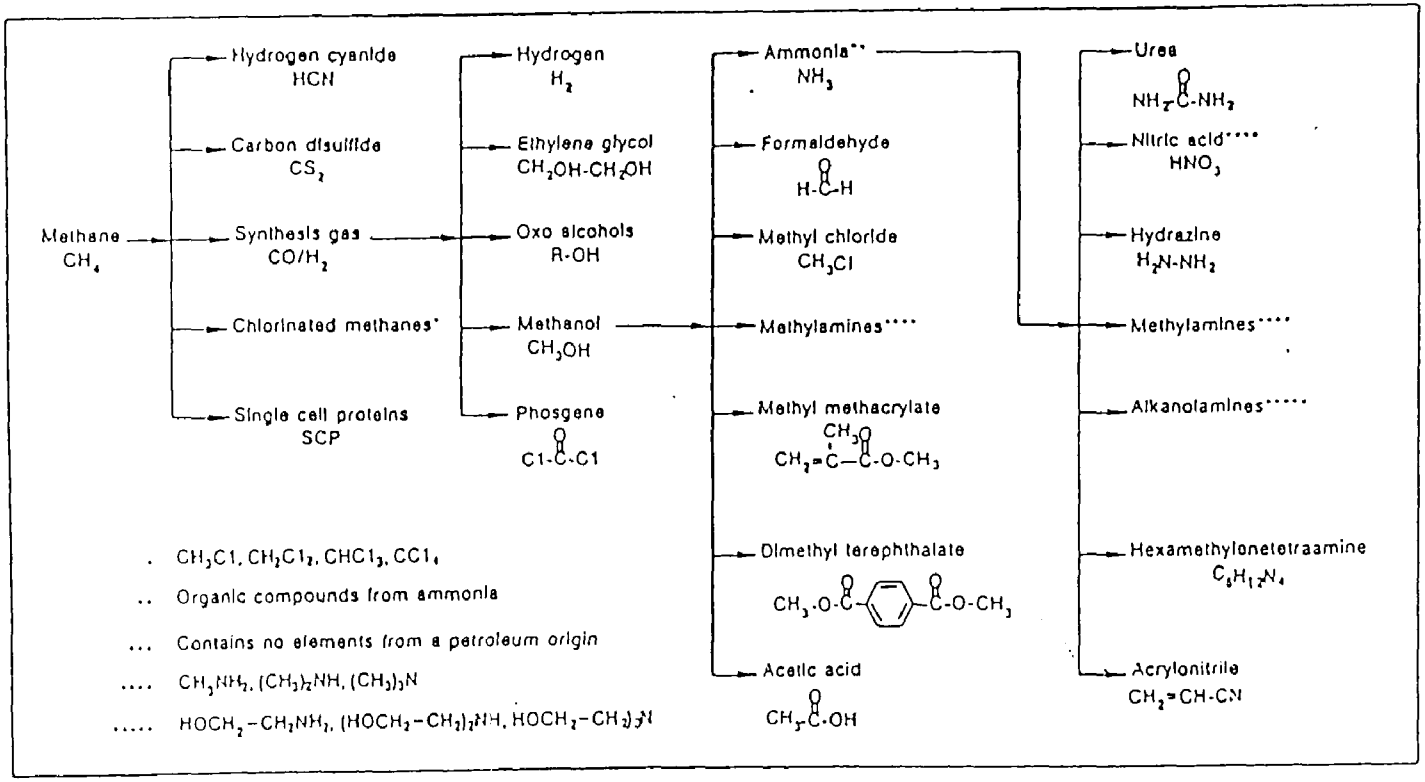
1. Carbon monoxide/hydrogen (synthesis gas) from reforming natural gas.
2. Alkenes from pyrolysis of ethane, propane-butane or distillates.
3. Aromatics from catalytic reforming.

For example, a producer of basic petrochemicals could consider natural gas as his only raw material and synthesis gas (CO/H_2), after conversion to methanol, as his finished product. An intermediate producer uses the merchant methanol as raw material to produce formaldehyde as a finished product while a resin manufacture would see the formaldehyde as a basic raw material for the production of phenolformaldehyde resins[2].

Natural gas (methane) is the precursor of a wide variety of compounds as shown in figure 1. Hydrogen which is produced from reforming natural gas combined with atmospheric nitrogen is used for the production of ammonia. Ammonia is the parent compound of many chemicals especially compounds used as fertilizers. Process gas with appropriate ratio of carbon monoxide to hydrogen is used to produce methanol and other alcohols including ethylene glycol and other chemicals. Methanol is a precursor for a host of other important chemicals such as formaldehyde, acetic acid, dichloromethane, and methylamines (see figure 1).

Figure 1. Major compounds derived directly or indirectly from methane.

Many of these compounds also have other raw material sources.



5.2 *Objectives*

Three sets of impurities were supplied for analysis from : a urea plant, a methanol plant and a sample from the Sahel oil field. The operation of the two petrochemical plants will be described separately.

The methods of sampling and analysis described in British Standards[3] are intended to cover a complete investigation of deposits in cooling systems, boilers, condensers, turbines and heat exchangers of any industrial plant involving heat transfer. These deposits can occur on the water or steam side of the following examples : boilers , feed systems, steam turbines, condensers or cooling systems.

The following definitions relate to British Standard[3]:

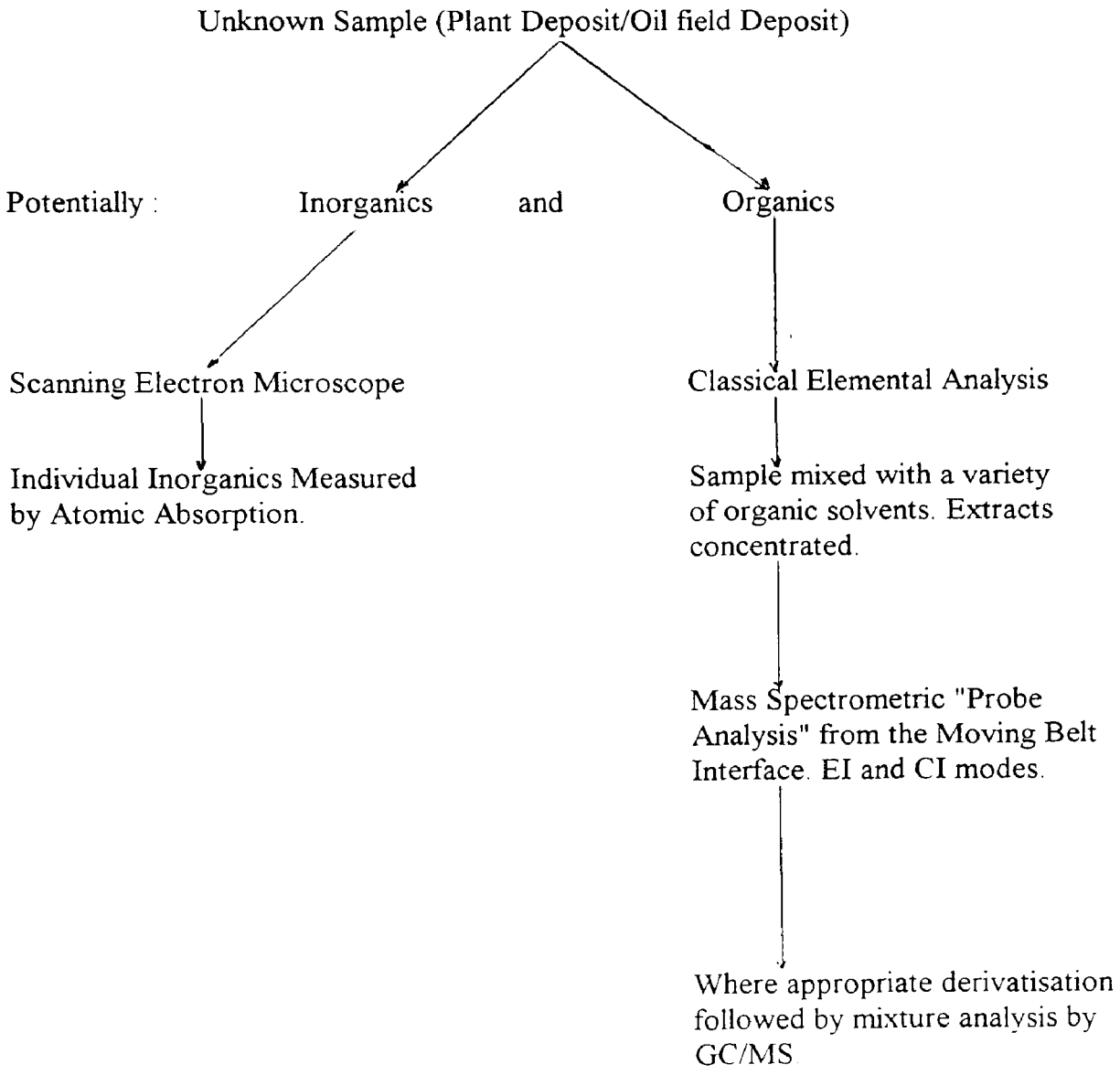
(a) Deposit - any adventitious material that occurs on the plant surfaces in the water or steam spaces.

(b) Sludge - a suspension in water of solid material that may form a deposit.

(c) Scale - a coherent deposit that adheres to, or has adhered to and subsequently broken away from, the surface on which it formed.

In order to characterise these impurities with respect to inorganic and organic constituents a general methodology was devised and is summarised in figure 2.

Figure 2. Strategy For The Analysis Of The Unknown Petrochemical Deposits.



5.3 *Urea Plant Operation*

Urea is used as a fertilizer and also as an important starting material for the manufacture of certain synthetic resins[4]. The process specific to the urea plant from which the contaminant was obtained can be summarised by the following stages :

The first stage involves the production of ammonium carbamate by the high pressure, high temperature reaction of excess ammonia with carbon dioxide[5]. In essence, the production of urea involves two stages. The first is the condensation of gaseous ammonia and CO_2 at high pressure and temperature[6]. The reaction is as follows :

$$CO_2(g) + 2NH_3(g) = NH_2CO_2NH_4(g)$$

In this first step, ammonium carbamate is formed by an exothermic reaction.

In the second stage of the reaction the ammonium carbamate dehydrates to produce urea. In this step the conversion of carbamate to urea is of the order of 50 to 75 per cent[7].

$$NH_2CO_2NH_4(g) = NH_2CONH_2(g) + H_2O(g)$$

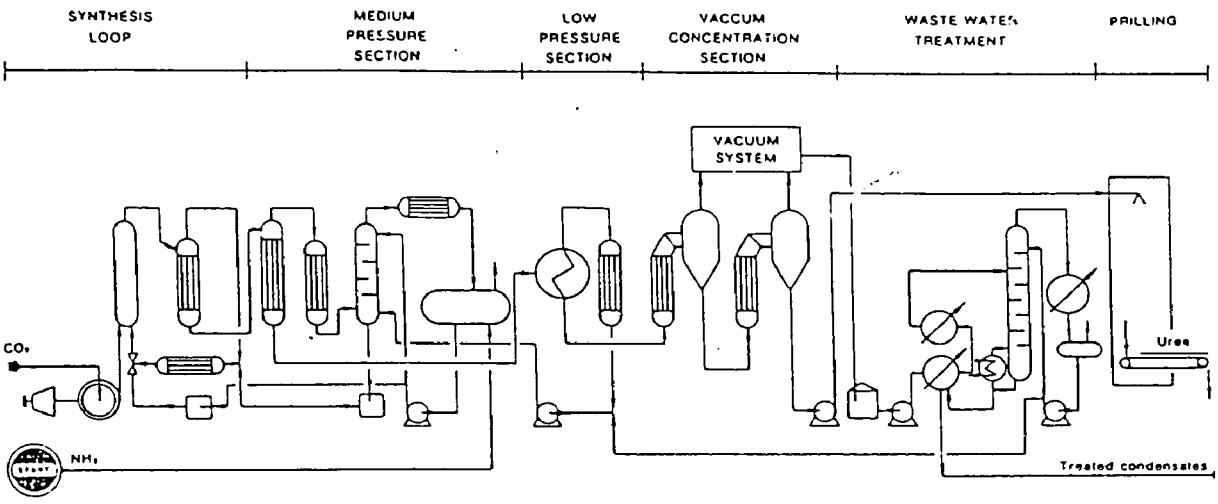
The exact details of the urea plant operation will now be described below.

During the first stages of the process ammonia and carbon dioxide in a ratio of about 3 moles to 1 mole are compressed and charged separately into a steam heated, silver-lined autoclave which serves as the reactor.

The reaction requires approximately two hours during which time the autoclave is maintained at a temperature of approximately 190 °C and pressure of 1500 to 3000 psi[8]. During this time the ammonia and carbon dioxide react to form ammonium carbamate and some urea. The reaction mixture at this stage consists of about 35 per cent urea, 8 per cent ammonium carbamate, 10.5 per cent water and 46.5 per cent unreacted ammonia.

This reaction mixture is then discharged from the autoclave and cooled to approximately 150 °C. The mixture is then passed to an ammonia still, operating at 60 °C, where 60 per cent of the unreacted ammonia and any unreacted carbon dioxide are distilled and collected in an ammonia - absorption system. The absorbed materials may then be reused in the reactor. At this stage the remaining reaction mixture is composed of approximately 50 percent urea. About 70 per cent of the remaining free ammonia is removed by vacuum and sent to a recovery system. Following this stage the reaction mixture now consists of approximately 70 per cent urea. The resulting reaction mixture is then fed to an injection system held under vacuum which is designed to primarily remove water. Following this step a hot concentrated solution of urea (approximately 99.7 percent by weight) is directed towards a Pilling tower where pellets of urea are produced. At the top of the Pilling tower an industrial centrifuge arrangement, operating at approximately 250 rpm, sprays the urea solution into the stack whose interior temperature is not greater than 70 °C. The base of the tower is serviced by a compressed air supply which is directed upwards. Process pellets of urea are collected from the tower base. The centrifuge at the top of the tower has a conic shaped profile and the substance for analysis was found deposited at the base of the centrifuge[5] . The process of urea production is summarised in figure 3. In the above process a small quantity of oxygen is used to reduce corrosion. The temperature of the plant is also carefully controlled to minimise the decomposition of urea to biuret. The specification of urea produced by the above is such that the final product must contain less than 1 percent biuret.

Figure 3. Process of Urea Production.



5.4 *Analysis of Precipitate from Urea Plant*.

The sample from the urea plant was a white, flakey solid and was odourless. The sample was only sparingly soluble in hexane, methanol, benzene, dichloromethane, acetone and tetrahydrofuran. It's melting point was 220 °C and it's density was determined as 0.363g per cm^3.

The deposit was analysed by scanning electron microscopy (Cambridge, UK) in order that the overall elemental composition, particularly with respect to the inorganic species could be determined. The result of this analysis is shown in figure 4 with only aluminium, manganese and iron being found to be present. Following the initial SEM screening, quantitative atomic absorption studies were undertaken for each of the three elements identified by SEM. Since no signals could be detected for each of the three elements by atomic absorption it was concluded that aluminium, manganese and iron were present at only trace levels.

Classical elemental analysis indicated that the sample was composed of carbon 26.3%, hydrogen 5.9% and nitrogen at 40.8%.

The precipitate was then separately Soxhlet extracted with hexane and dichloromethane. Each extract was then concentrated by solvent stripping under a stream of nitrogen prior to GC/MS analysis. Figure 5 shows the results of the GC/MS analyses obtained for the Soxhlet hexane extract. The compound whose retention time was 4.9 minutes in the hexane extract was library searched , figure 6, and was identified as biuret (imidodicarbonic diamide) whose structure is as follows :

NH_2-CO-NH-CO-NH_2 $\quad M_r = 103$

The result of the library search for the compound whose retention time was 19.89 minutes is shown in figure 7. There are some similarities between the unknown compound's mass spectrum and that recorded for 2-nitro-thiophene, however 2-nitro-

Figure 4. Scanning electron microscope analysis of the deposit obtained from the urea plant.

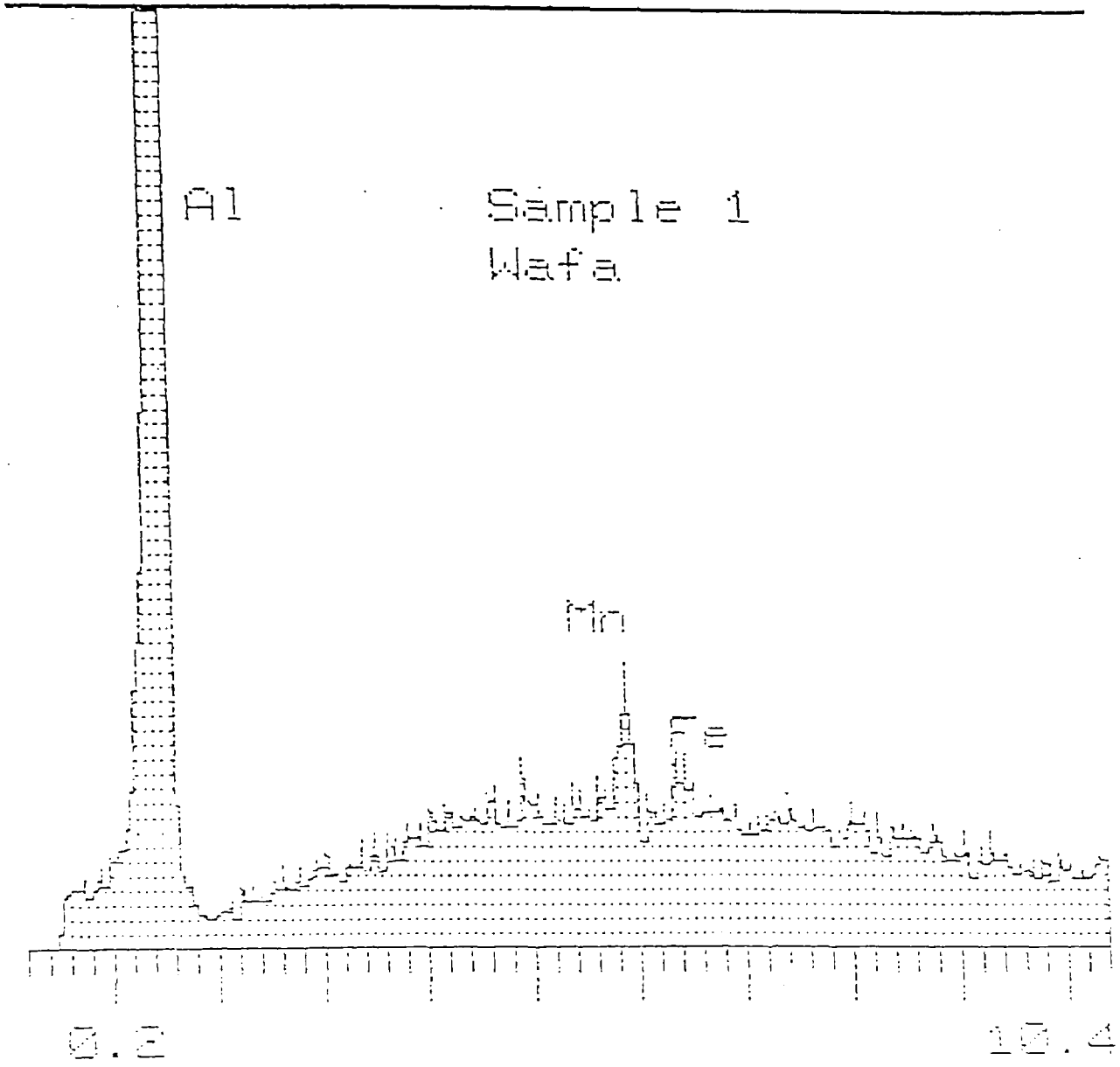


Figure 5. GC/MS analysis of hexane Soxhlet extract of urea plant deposit.

GC/MS conditions given in the appendix.

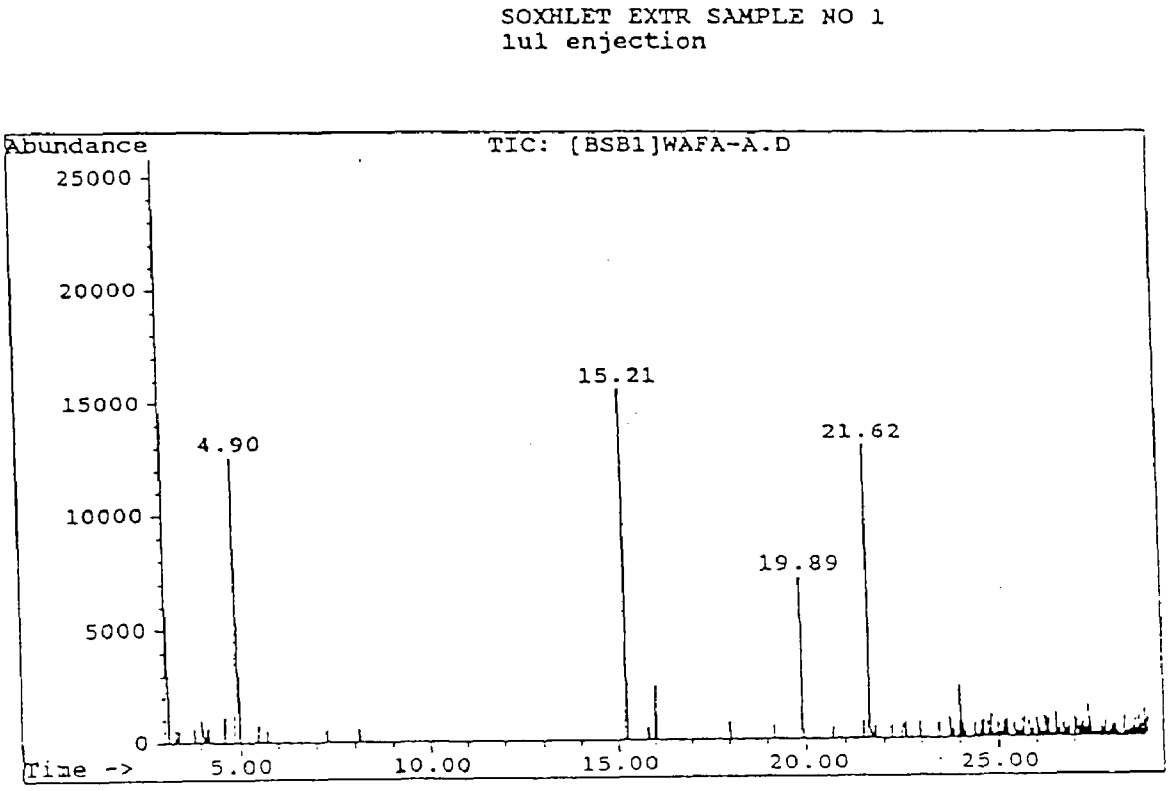


Figure 6. (a) Mass spectrum of compound whose retention time was 4.9 minutes when the hexane Soxhlet extract was analysed by GC/MS (see figure 5).

(b) Library search result obtained for the above compound.

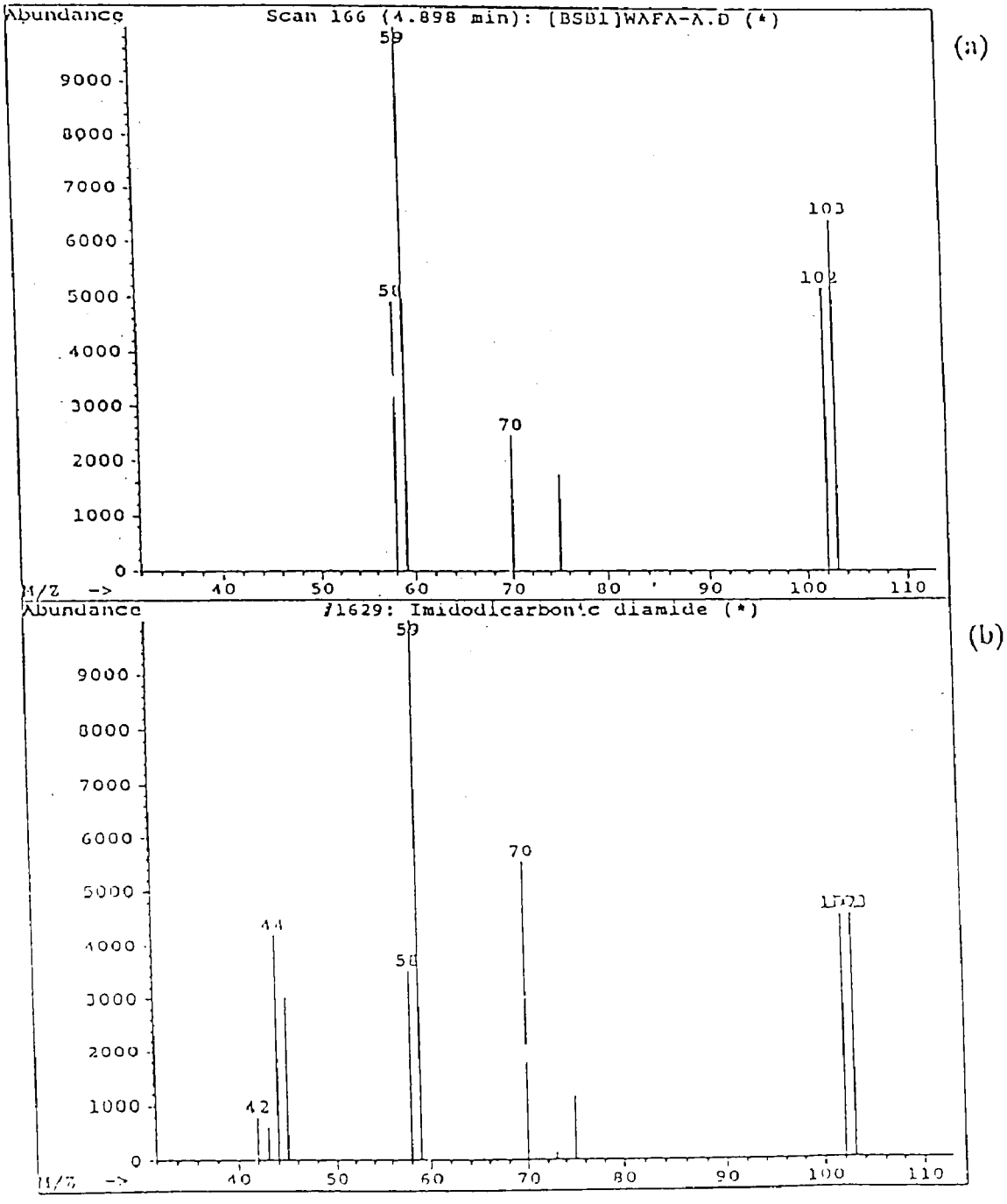
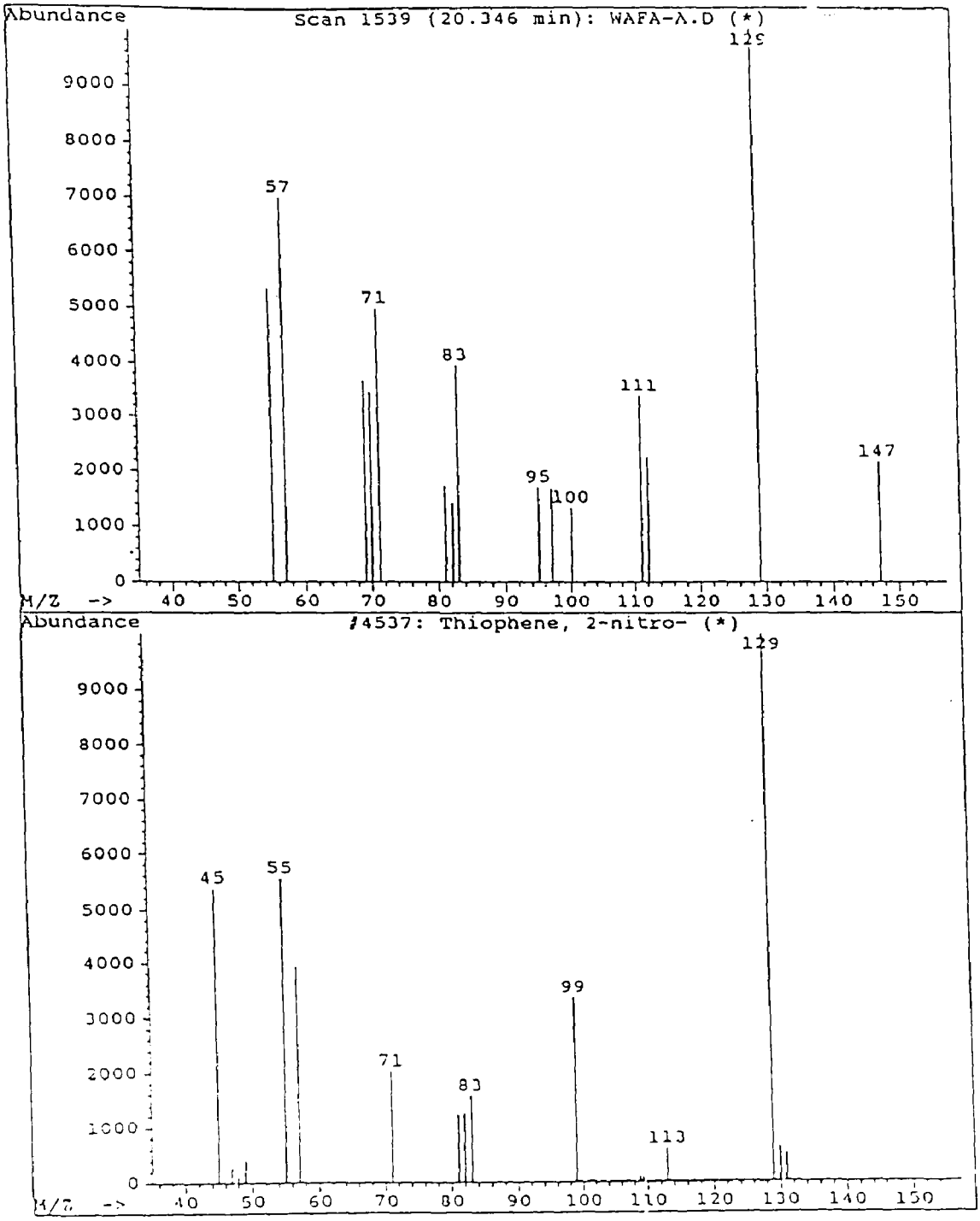


Figure 7. (a) Mass spectrum of compound whose retention time was 19.98 minutes when the Soxhlet extract was analysed by GC/MS (see figure 5).

(b) Library search result obtained for the above compound.



thiophene has a melting point of only 46.5 °C [9] whereas biuret has a melting point of 188-190 °C. Hence 2- nitro-thiophene was discarded as a possible contaminant based upon retention time values.

The compound whose retention time was 21.62 minutes was library searched as a phthalate and because of the wide range of sources where this class of compounds appear as contaminants no significance was attached to this result.

The Soxhlet extracted residue , used to provide the extracts for mass spectrometry, was air dried and a portion was used to make a potassium bromide disc for infrared analysis (Perkin Elmer, FTIR Model 1760, UK). The FTIR spectrum thus obtained is shown in figure 8. The spectrum is consistent of that for a non-aromatic amide since there is a very broad absorption positioned around 1620 cm^{-1}. Additionally there is a strong absorption centred around 3400 cm^{-1} and this is consistent with absorption in the region expected for primary and secondary NH_2 groups. A library search failed to identify the unknown compound following the FTIR analysis. The FTIR specrum for urea is shown in figure 9.

A sample of the deposit was agitated in the presence of ethanol and the supernatant liquid was applied to the moving belt interface under conditions of ammonia CI. Figure 10 shows the response that was obtained for two injections. Figure 11 shows the resultant ammonia CI mass spectrum obtained. Ions at m/z 61 and m/z 78 are most likely to represent the protonated and ammonium adduct ions of urea respectively. Ions at m/z 104 and m/z 121 are most likely to represent the protonated and ammonium adduct ions of biuret respectively. The ions at m/z 135 and m/z 152 are the characteristic 17 atomic mass units apart for a protonated and ammonium adduct molecular ion species. When the ion traces for m/z 104, m/z 121, m/z 135 and m/z 152 were examined, figure 12, it was found that m/z 135 and m/z 152 did not co-maximise with ions m/z 104 and m/z 121 and it was hence concluded that ions m/z 135 and m/z 152 were not related to the urea impurity profile.

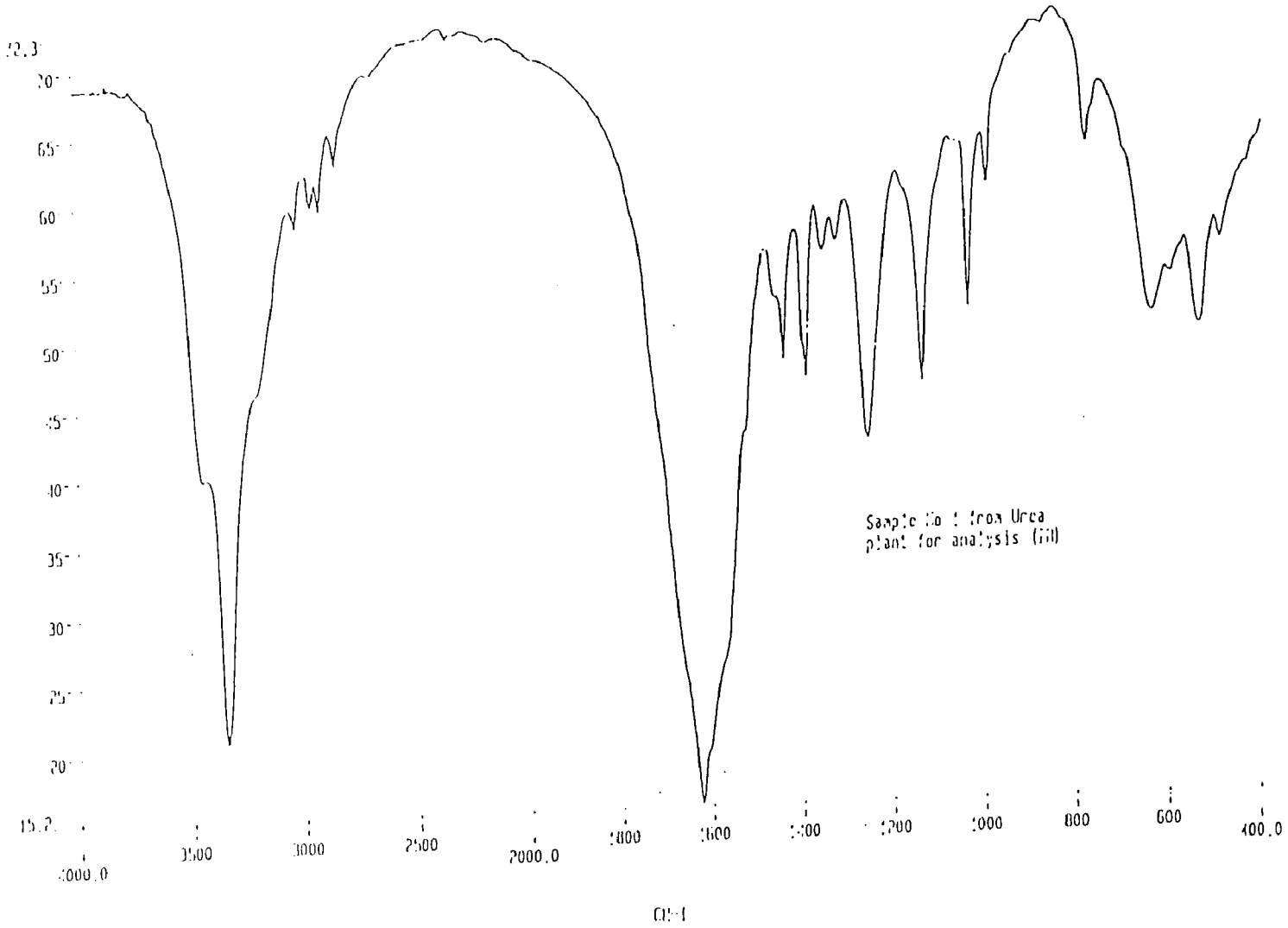


Figure 8. FTIR spectrum obtained for the deposit from the urea plant.

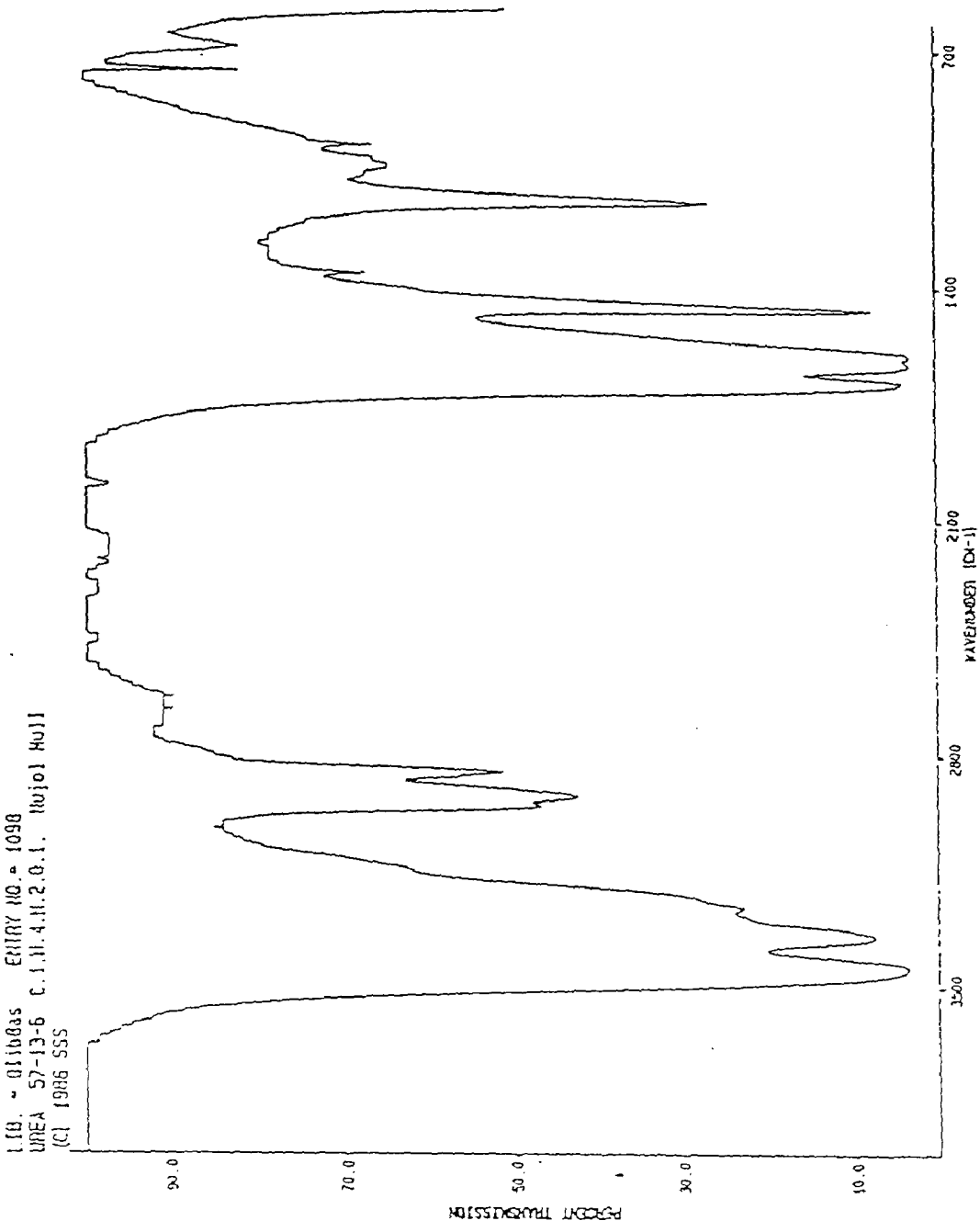


Figure 9. FTIR reference library search for urea.

Figure 10. Moving belt analysis of the supernatant ethanolic solution from the urea plant deposit. Two replicate injections made. Moving belt vaporiser temperature set at 200 °c. Ammonia CI.

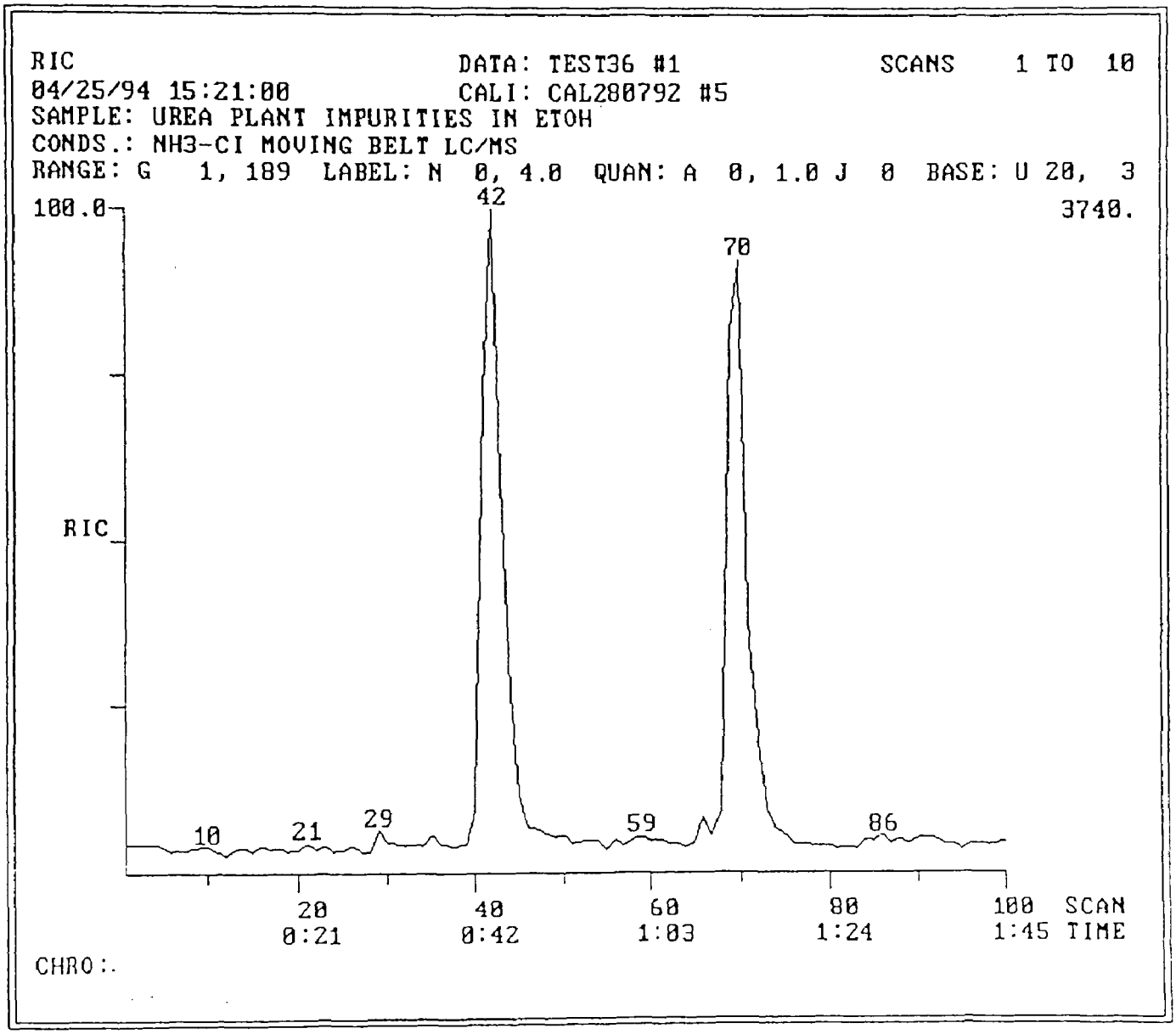


Figure 11. Moving belt ammonia CI mass spectrum obtained for the ethanolic extract of the urea plant deposit.

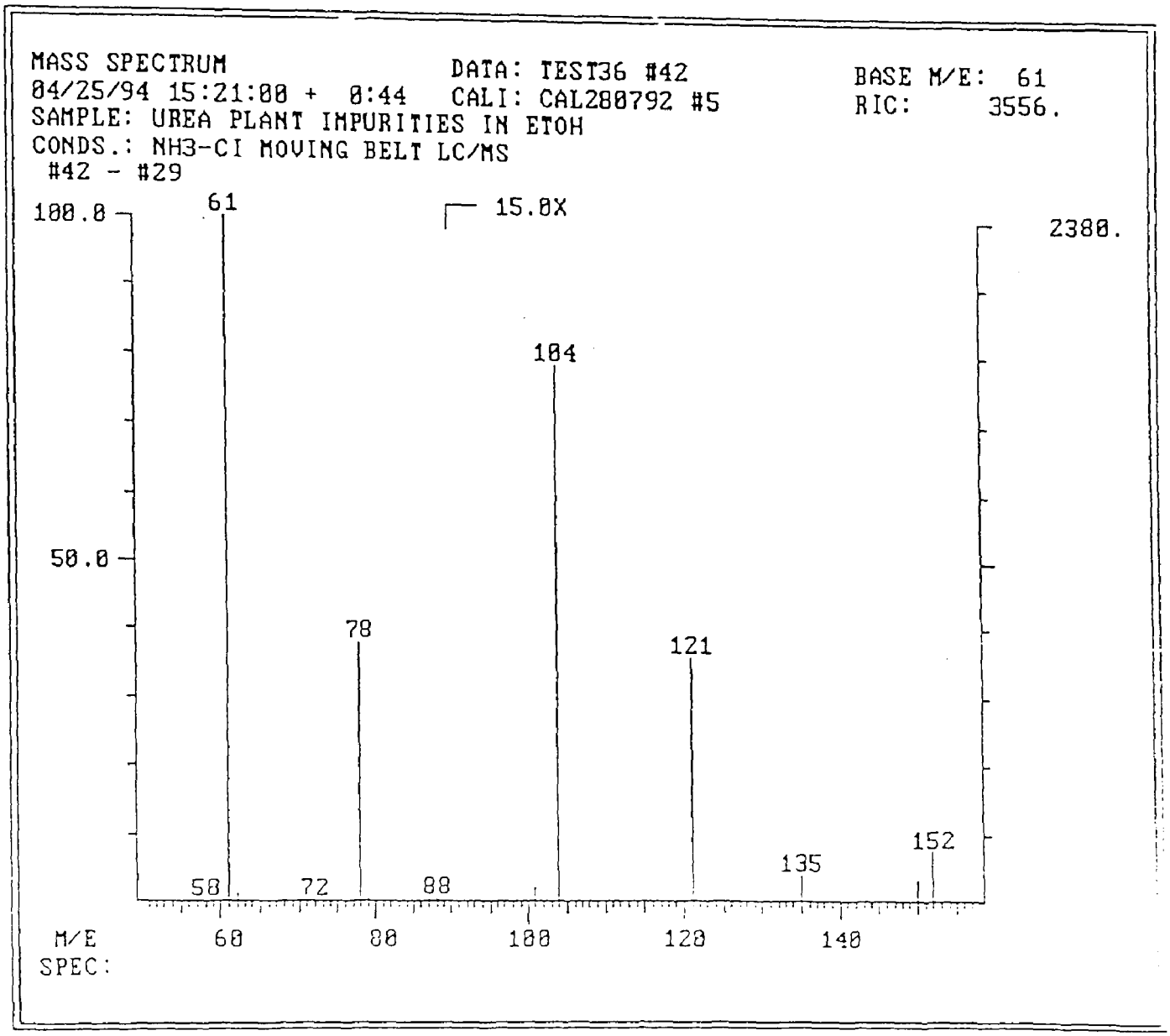
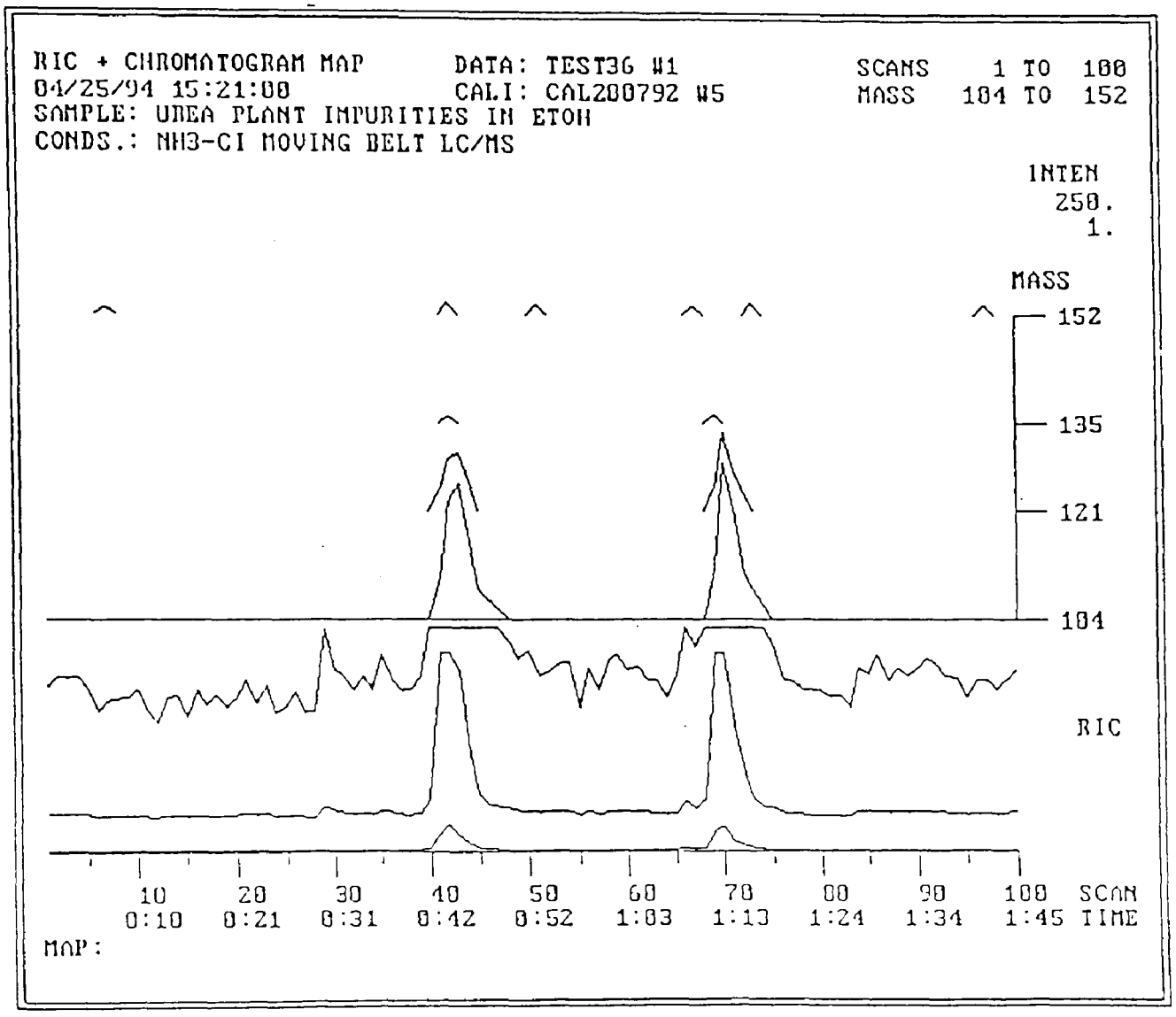


Figure 12. Ion chromatogram analysis of the ethanolic extract of the urea plant deposit. Analysis conditions as specified in figure 10.



5.5 *Discussion of results for the Urea Plant Deposit*

Since the deposit was found to be largely composed of organic material it was suprising that despite repeated attempts no organic solvent could be found to dissolve the sample.These observations resulted in early suspicions that the deposit was polymeric or oligomeric although the relatively low melting point did not help support this view. The first proposed structure for an oligomeric contaminant was :

(1) NH_2-CO-NH-CO-NH-CO-NH_2 $\quad M_r = 146$

This proposal was based upon the melting point recorded and the results of classical elemental composition which are tabulated below :

Table 1. Results of Classical Elemental Composition for the Deposit isolated from the Urea Plant.

		Expected Result		
Element	Recorded Result	Urea	Biuret	Proposed Structure(1)
Carbon	26.3%	20%	23.3%	25%
Nitrogen	40.8%	47%	40.77%	38%
Hydrogen	5.9%	6.66%	4.85%	4.1%

Given the accuracy with which these analyses can be undertaken the above figures appear acceptable for the proposed structure. Unfortunately lack of solubility does not tend to support the structure proposed. Mass spectrometric analyses indicated the presence of biuret in the sample although the relatively weak ion count for the GC/MS analysis strongly tends to indicate that this species does not form a significant part of the overall deposit composition. Urea and biuret could be detected by spotting the organic extracts onto the moving belt LC/MS interface

The FTIR results tend to indicate that the insoluble organic contaminant is a non-aromatic amide and supports the results of the elemental analysis since no appreciable C-H stretching was observed. Unfortunately the FTIR spectrum did not library search although manual inspection of reference spectra[10] supports the view that the unknown is an amide. Comparison of the FTIR obtained for the deposit and a urea standard again tends to bring the first proposed structure into doubt due to the lack of similarity of the urea primary $-NH_2$ stretches against that observed for the unknown compound. The most similar amide reference spectrum to that of the unknown is that of 5-aminobarbituric acid which is a six membered cyclic compound, consisting of three carbonyl groups and three secondary -NH functions ($C_3H_3O_3N_3$, M_r = 129). However if the unknown compound had a similar structure to 5-aminobarbituric acid it should be highly soluble in a variety of organic solvents and also the theoretical elemental composition of 5-aminobarbituric acid of: carbon 27.9%, nitrogen 32.5% and hydrogen 2.3 % is far removed from that actually recorded (see table 1).

Perhaps the best way forward to further study this deposit from the urea plant would be to obtain accurate molecular weight information. The lack of solubility in suitable organic solvents in this case limits the use of the moving belt interface for this sample although the low melting point means that the sample should be amenable to direct insertion probe analysis. The use of surface ionisation techniques such as fast atom bombardment may also be of value in obtaining molecular weight information particularly in the event that the impurity is a high molecular weight polymer.

5.6 *Methanol Plant Operation*

The process whereby methanol is produced within the Sirte Oil Petrochemical Complex can be summarised by the following equation :

$$CO(g) + 2H_2(g) = CH_3OH^{(l)}$$

The synthesis reaction requires a molar ratio of hydrogen to carbon monoxide of 2 : 1, whereas the steam reforming process of methane, within the complex, gives a gas with a ratio of 3 : 1. The gas ratio is adjusted by adding carbon dioxide to the reformer feed[11], which is then converted within the reformer to produce carbon monoxide according to the following equation :

$$CO_2(g) + H_2(g) = CO + H_2O(g)$$

This process is controlled such that the correct ratio of hydrogen and carbon monoxide will be reacted to produce methanol. Other steps involved in the process include desulphurisation and reforming[12].

The Sirte Petrochemical plant is fed by the Hatiba and Sahel gas fields. The incoming natural gas contains sulphur that is removed by passing the compressed gas into a heated desulphurisation (H.D.S.) unit that uses copper (II) oxide as catalyst. The H.D.S. unit also removes chlorine and sulphur containing compounds.

The natural gas product now largely consists of methane (80%) and other alkanes up to C-5 as well as nitrogen, carbon dioxide and hydrogen. This gas is then passed to a preheater unit and from there to a reformer situated in the methanol plant. At this stage the gas is mixed with steam which is also supplied to the reformer. The reformer is composed of 450 tubes which are held at a temperature of 850 °C and contain nickel (II) oxide as catalyst. The reformer tubes are also supplied with compressed make-up gas (msg) which is composed of argon, nitrogen, carbon monoxide, hydrogen and methane.

At this stage the natural gas is cracked to produce a product enriched with respect to carbon monoxide, carbon dioxide and hydrogen. The gas mixture then leaves the reformer and is passed to a converter where the carbon monoxide and hydrogen mixture is compressed to produce crude methanol. The crude methanol is purified by fractional distillation and finally filtered to produce the product. The Sirte Oil product specification requires the methanol to be 99.99% pure when assayed by gas chromatography.

The deposit to be analysed from the methanol plant was obtained from the filter elements from the distillation tower.

5.7 *Analysis of the Deposit Obtained from the Methanol Plant*.

The sample from the methanol plant was a waxy solid. The solid showed a wide range of particle sizes and the particles exhibited a range of colours ranging from dark kharki to grey interspersed with black fragments. The solid was odourless and was found to be soluble in hexane, methanol and acetone. It's melting point was determined between 40-50 °C.

The volatility of the sample prevented its analysis by SEM. Atomic absorption studies failed to indicate the presence of the following elements[13] : aluminium, iron, manganese, nickel, chromium, zinc, copper, magnesium, lead, sodium, potassium, calcium, sulphur, nitrates and chlorine.

The results of classical organic elemental composition resulted in the following :

Table 2. Results of classical elemental analysis for methanol plant impurity.

Element	Percentage
Carbon	85%
Hydrogen	15%
Nitrogen	0%
Iron	2.4 ppm

Hence the results of the above analyses strongly indicate that the methanol plant deposit is largely composed of hydrocarbons and consequently was subjected to GC/MS analysis. The result of GC/MS analysis is shown in figure 13 and all spectra obtained indicated that the deposit was composed of a homologous series of hydrocarbons.

5.8 *Discussion of results for the methanol plant Deposit*

Results of the classical elemental and GC/MS analyses clearly indicate that the waxy deposit is composed of a homologous series of hydrocarbons. In order to estimate carbon chain length a known homologous series of alkanes was analysed by GC/MS and the retention times were used to estimate carbon chain length. The result of the GC/MS analysis of the standard hydrocarbon mixture (from C-12 to C-20) is shown in figure 13 and comparison of the retention times for figures 13 and 14 revealed that the methanol plant deposit was a homologous series of hydrocarbons whose chain length varies from C-12 to C-33. The melting point range recorded for the sample is consistent with these findings.

Fifure 13. GC/MS analysis of standard hydrocarbon mixture ranging from C-12 to C-20. GC/MS conditions in the appendix.

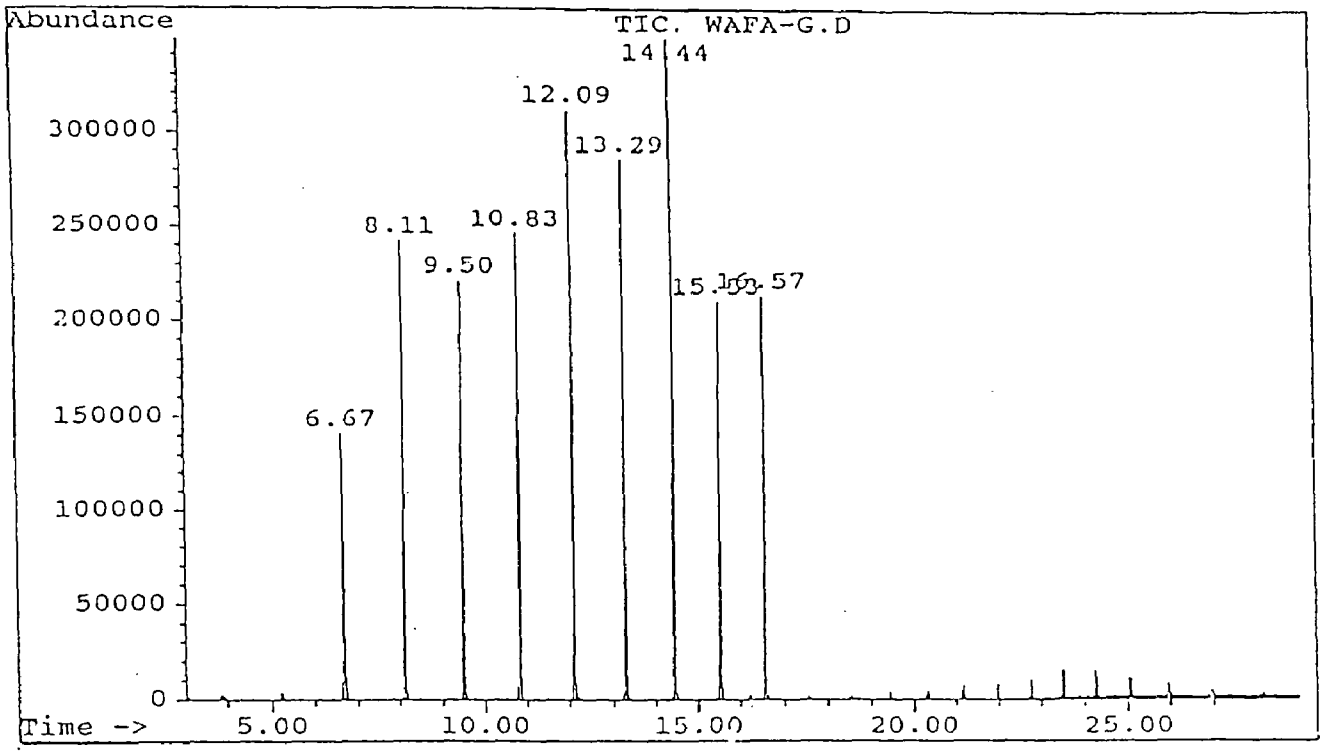
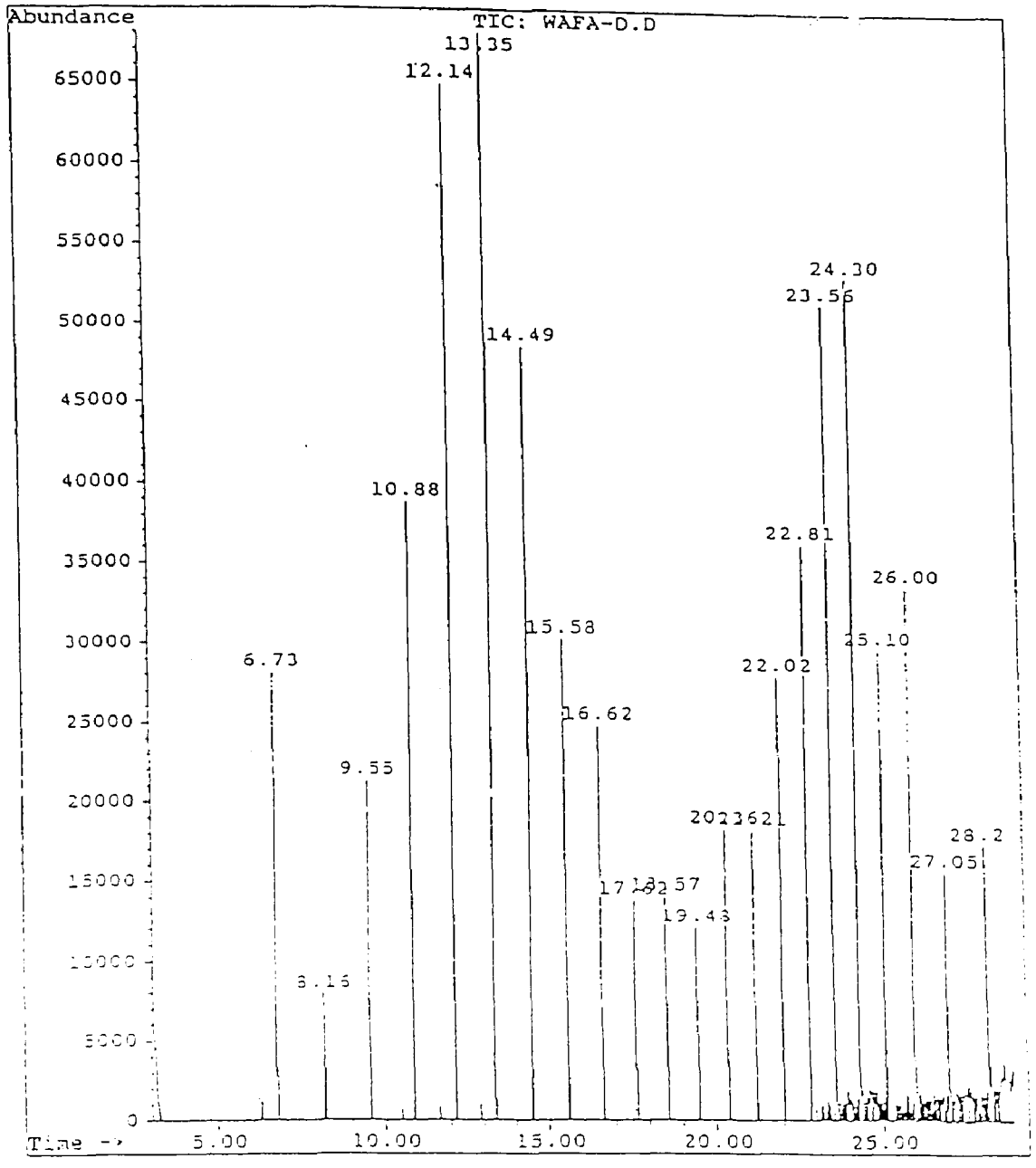


Figure 14. GC/MS analysis of a methanolic solution of the deposit obtained from the methanol plant. GC/MS conditions given in the appendix.



5.9 *Sahel Gas Field*

The sample submitted for analysis came from the quality assurance laboratories of the Sirte Oil company, unfortunately no further information was provided as to where the sample was precisely obtained from the Sahel gas field.

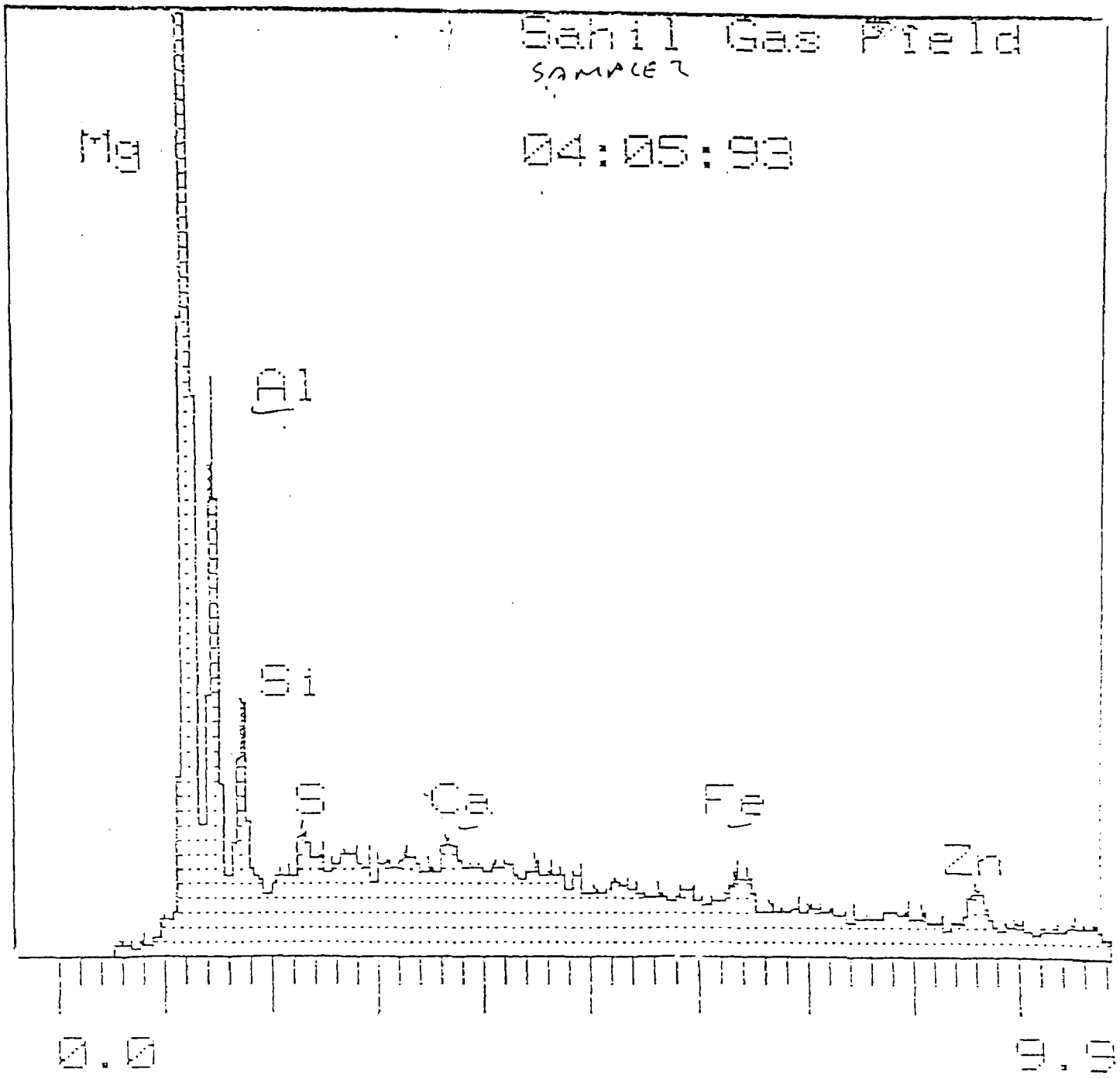
5.10 *Analysis of the deposit obtained from the Sahel gas field*.

The sample from the Sahel gas field was particulate. The particles showed a variety of colours ranging from white through a series of different grey colours. The solid was sparingly soluble in tetrahydrofuran, hexane, methanol and dichloromethane. The solid was however soluble in several mineral acids including concentrated sulphuric and nitric acid. The result of SEM analysis is shown in figure 15 and clearly indicates the presence of magnesium, aluminium, silicon, sulphur, calcium, iron and zinc. The results of atomic absorption analysis are tabulated in table 3.

Table 3. Atomic absorption results for Sahel gas field deposit.

Element	Percentage Composition by Mass
Magnesium (as MgO)	31.25 %
Aluminium (as Al_2O_3)	6.7 %
Silicon (as Silica)	5.0%
Sulphate (as SO_4^{-2})	0.32%
Calcium (CaO_2)	0.20%
Iron (as Fe_2O_3)	0.30%
Zinc(as ZnO)	0.37%
Manganese (as MnO_2)	0.13%
Copper (as CuO)	0.038%
Chlorine	0.24%
Nitrate (as NO_2)	0.24%
Lead	0.03%

Figure15. Scanning electron microscope analysis of the deposit obtained from the Sahel gas field.



The results of classical organic elemental analysis are shown in table 4.

Table 4. Results of classical organic elemental analysis for the deposit obtained from the Sahel gas field.

Element	Percentage
Carbon	4.8 %
Hydrogen	3.4 %
Nitrogen	0 %

The deposit was subjected to Soxhlet extraction with hexane. The resultant extract was concentrated and then subjected to analysis by GC/MS whose result is shown in figure 16. The compounds whose retention times were 15.31 minutes, 16.31 minutes and 20.05 minutes were all identified with a high degree of confidence as phthalates and no significance was assigned to these findings. The compound whose retention time was 4.313 minutes was library searched , figure 17, and was identified as 2-ethyl, 1-hexanol. The library search result for the compound whose retention time was 18.84 minutes is shown in figure 18. Although doubt exists about the library search result for the compound whose retention time was 18.84 minutes, if m/z 270 is the molecular ion then the isotope pattern is consistent for the presence of two atoms of chlorine in the molecular species.

Figure16. GC/MS analysis of hexane Soxhlet extract of the Sahel gas field deposit. GC/MS conditions given in the appendix.

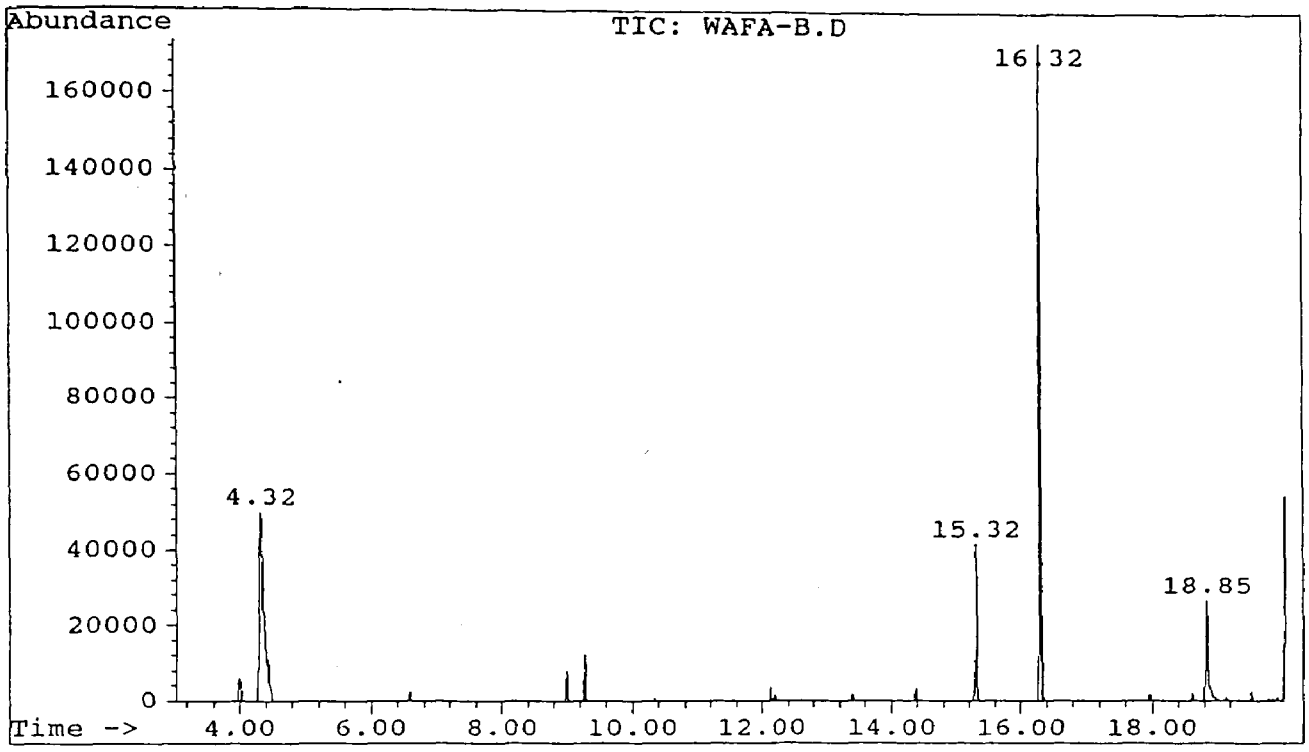


Figure 17. (a) Mass spectrum of compound whose retention time was 4.313 minutes when the hexane Soxhlet extract of the Sahel gas field deposit was analysed by GC/MS (see figure 16).

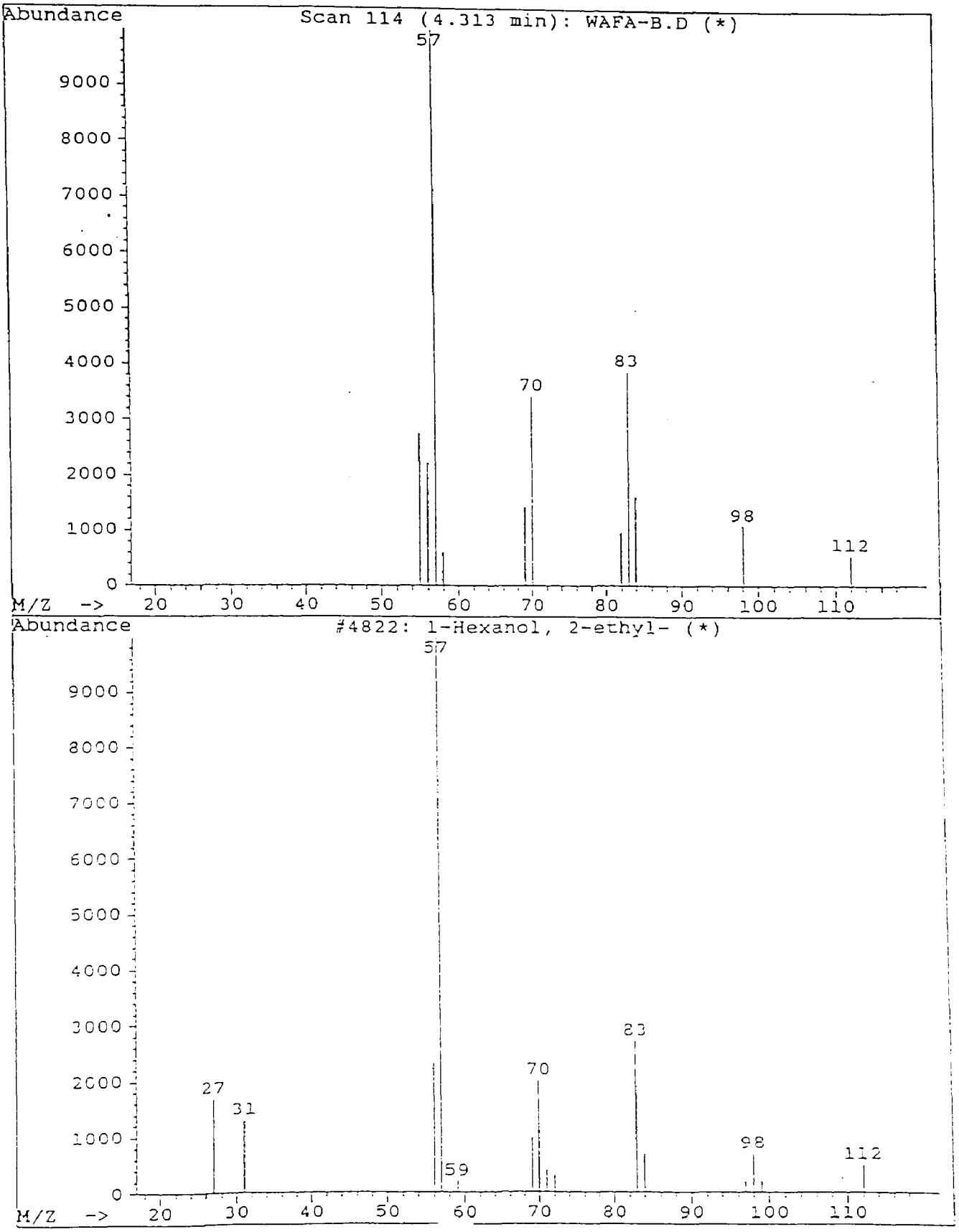
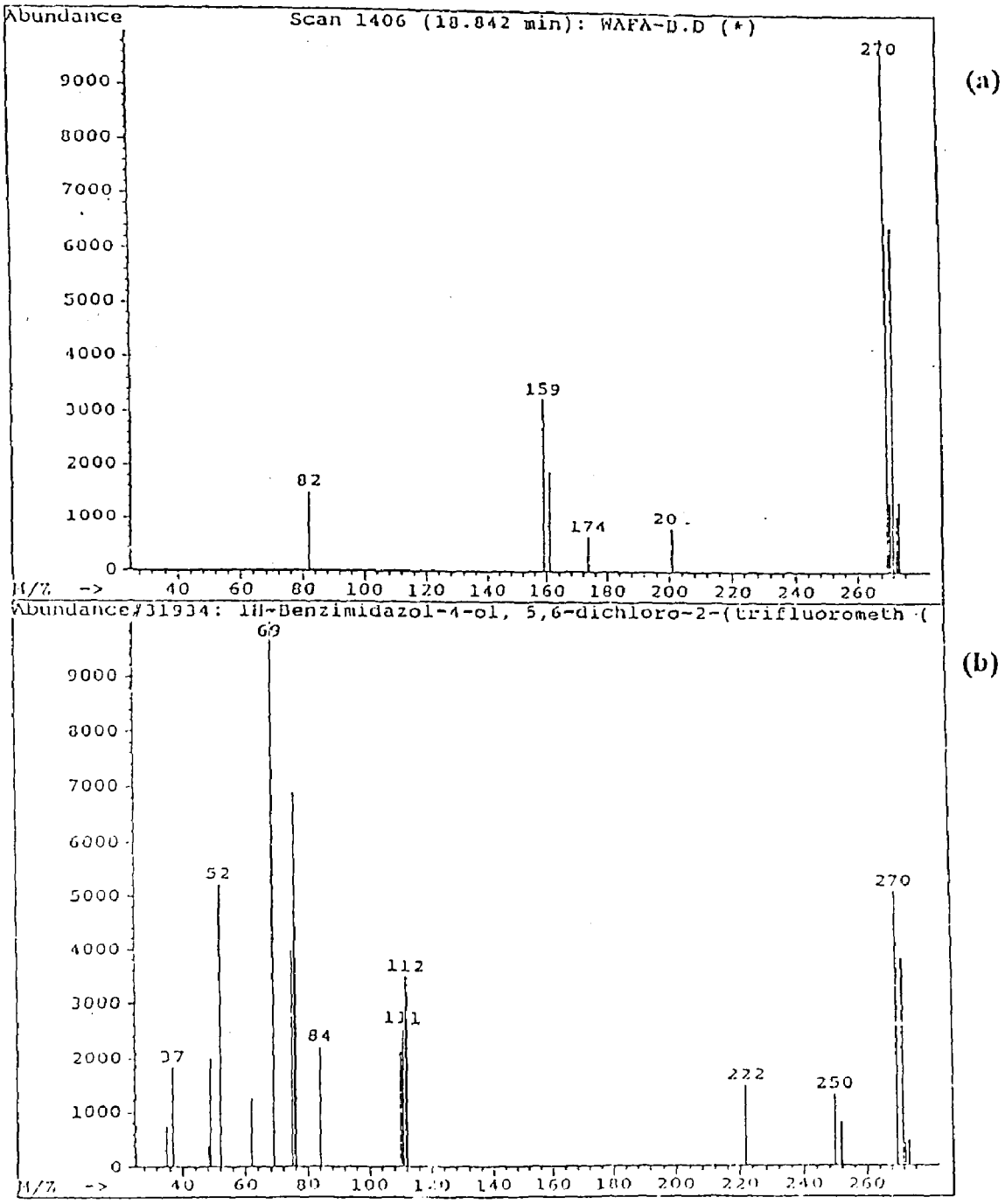


Figure 18. (a) Mass spectrum of the compound whose retention time was 18.84 minutes when hexane Soxhlet extract of the Sahel gas field deposit was analysed by GC/MS (see figure 16).

(b) Library search result obtained for the above compound.



5.11 *Discussion of results for the Sahel gas field Deposit*

The deposit from the Sahel gas field largely consists of inorganic species and is particularly rich in magnesium and aluminium compounds. The results of the classical organic analyses suggest that only a small quantity of organic compounds are present and the results of the GC/MS analysis strongly suggest the presence of 2-ethyl, 1-hexanol and a molecular species which contains two chlorine atoms. The relatively high carbon to hydrogen ratio following the classical elemental analysis is accounted for by the fact that carbonate was reported as being present, see appendix 5, this is substantiated by the observation that there is slight effervescence when the impurity is dissolved in mineral acids. Without further precise details of the sampling point it is difficult to make further comments.

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Appendix

Contents

File Control Segment Parameters Configuration Exit

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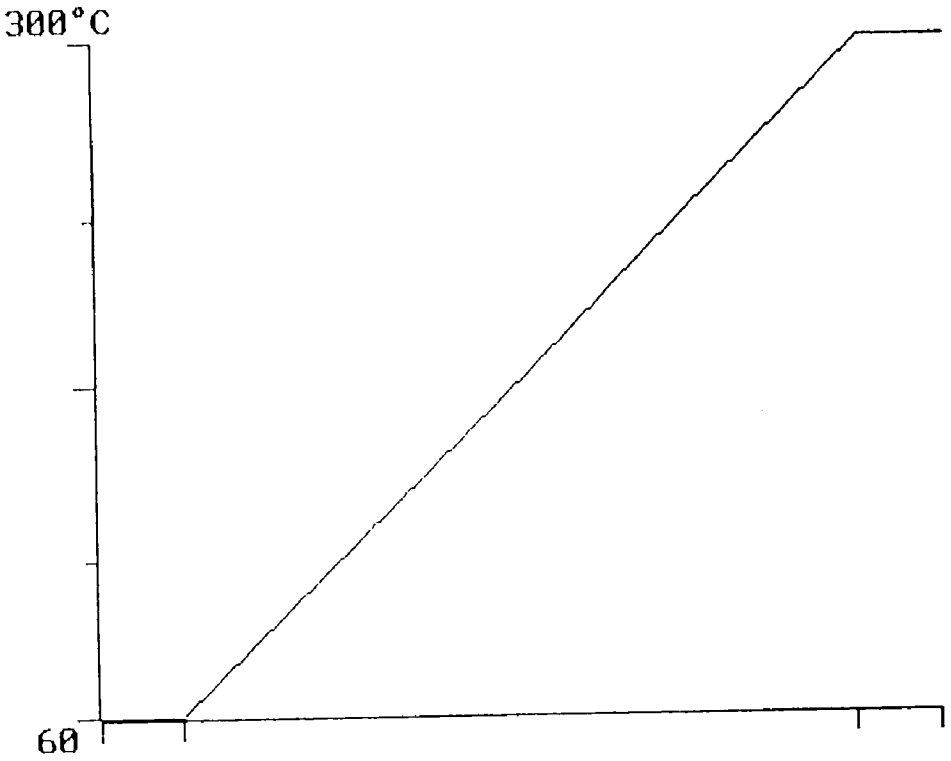

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2	300	10.0	24.00	27.00
3	300	0.0	3.00	30.00

Start 60 °C

End 60 °C

Rate 0.0 °C/min

Time 3.00 min

Valve 1

Valve 2

	Column	Injector	Xfer Line
Set	60 °C	260 °C	270 °C
Actual	40 °C	50 °C	60 °C

For appendix 2 GC condition used for the analysis of PAH's shown in (figure 7-12).

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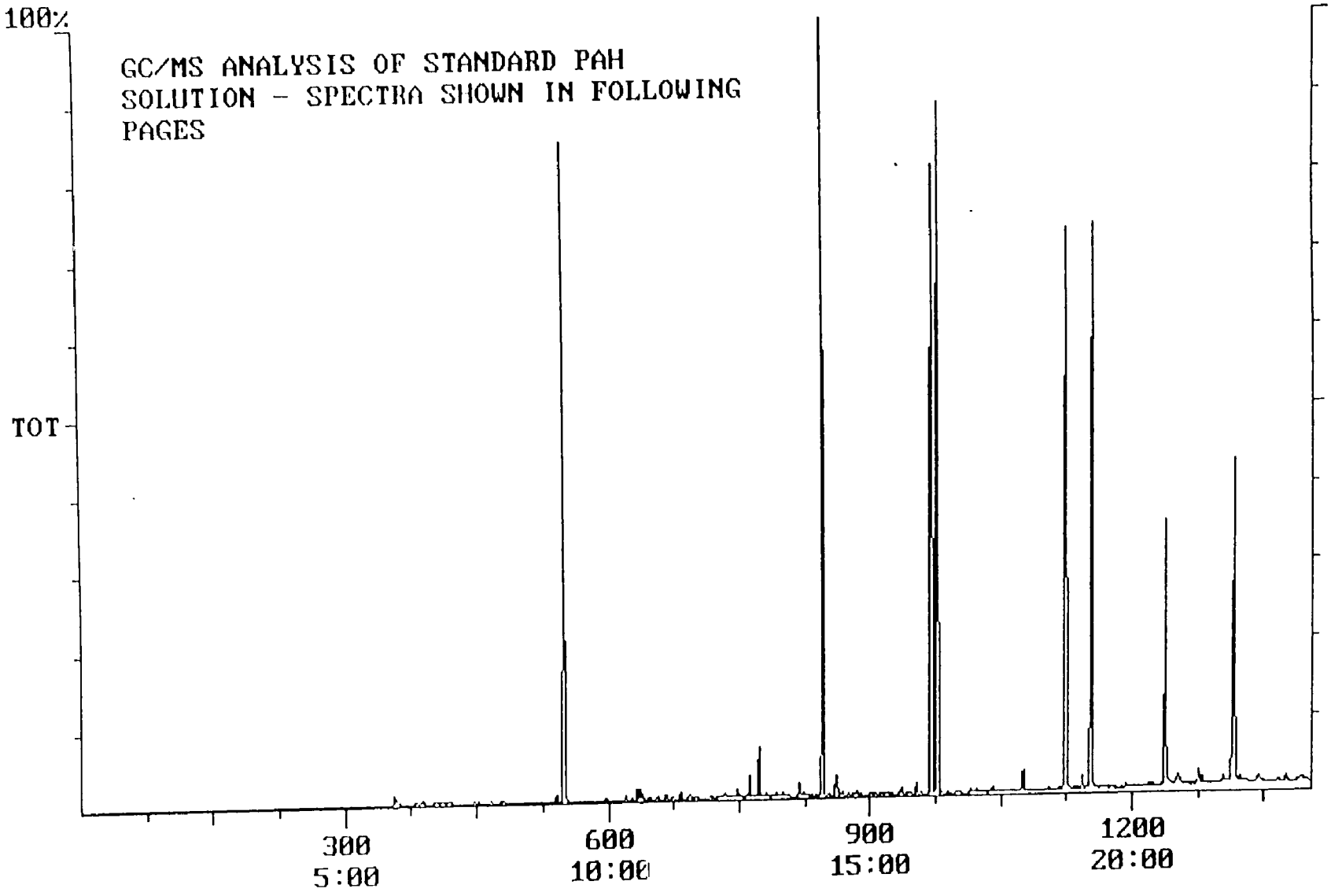

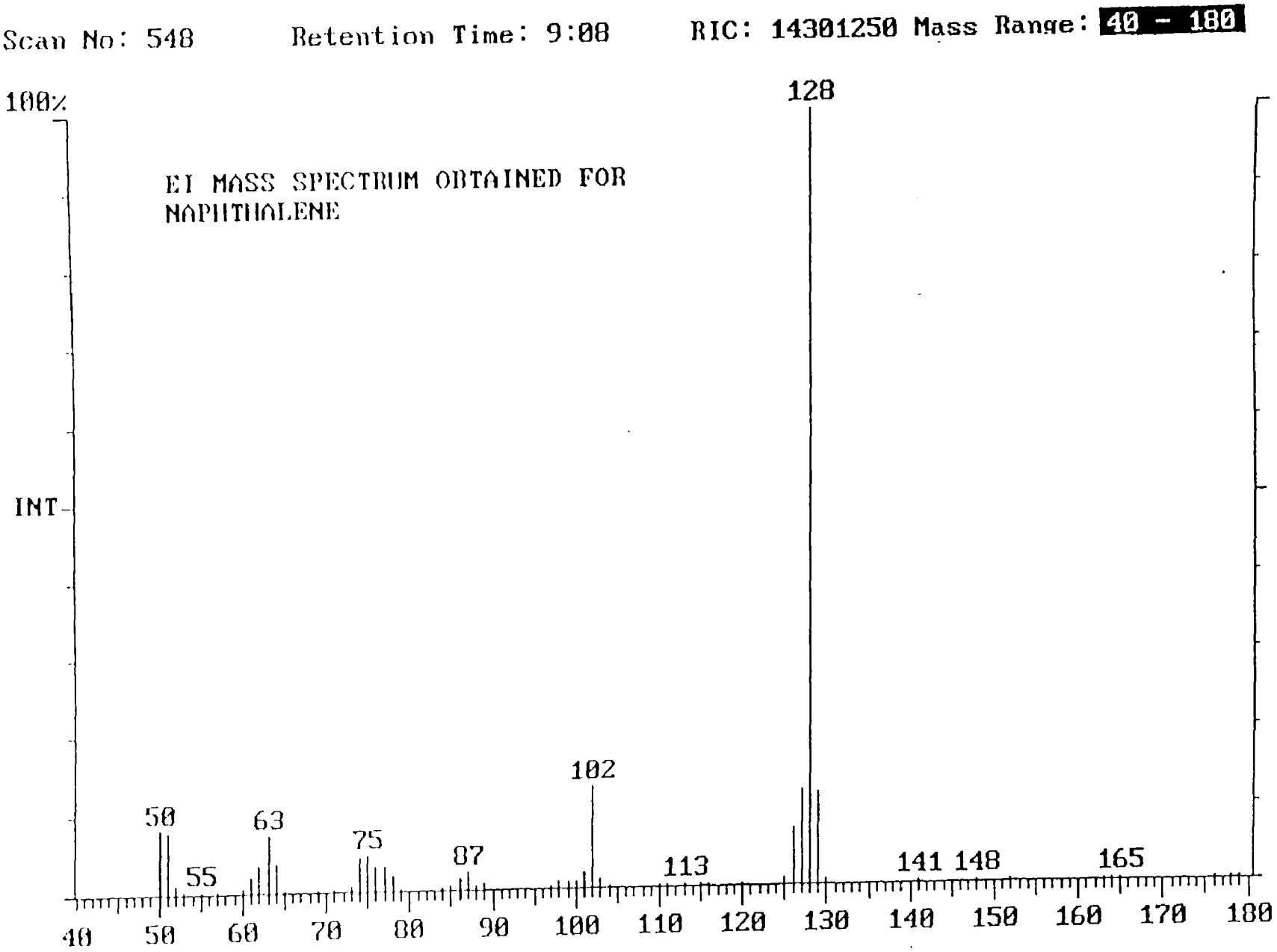
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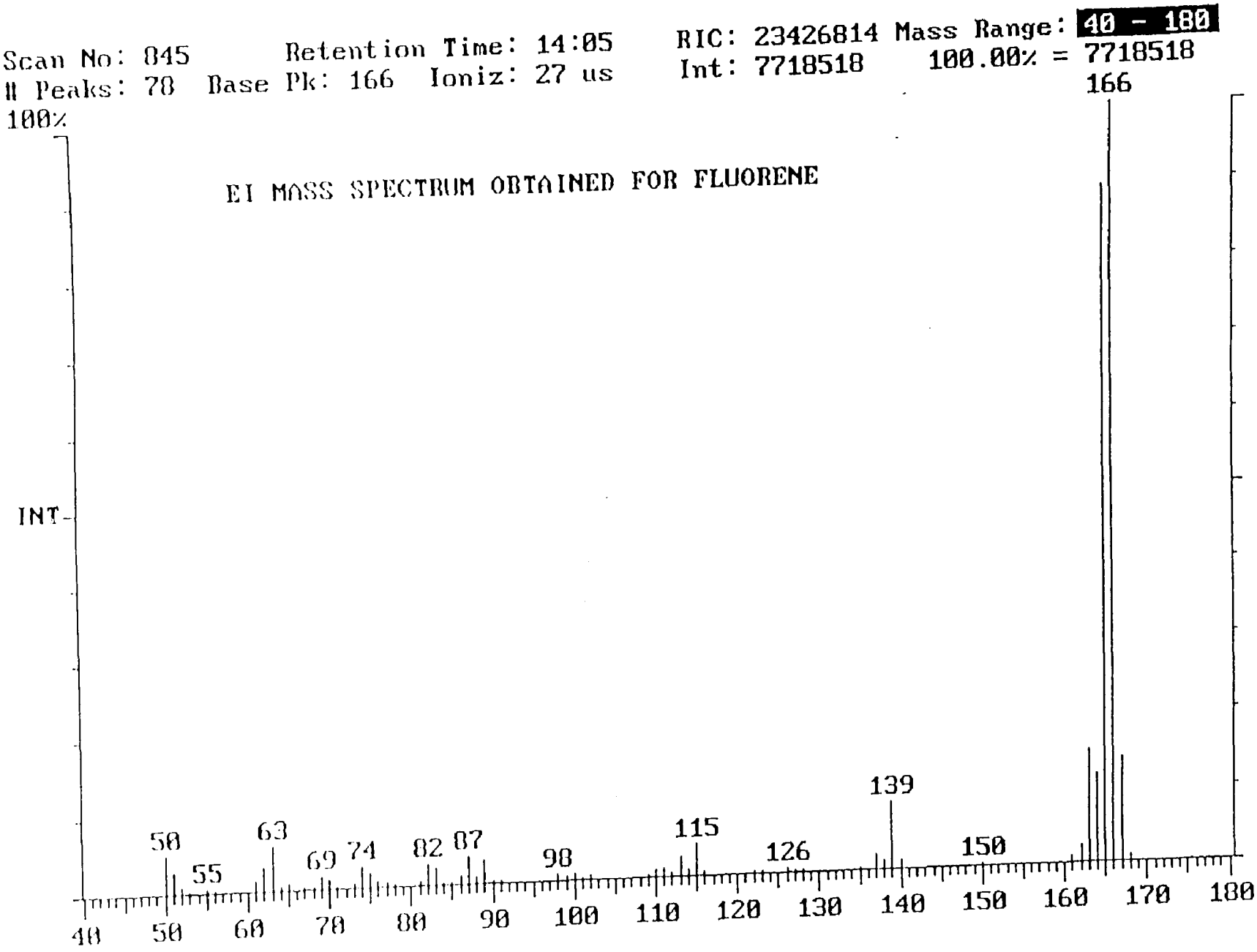
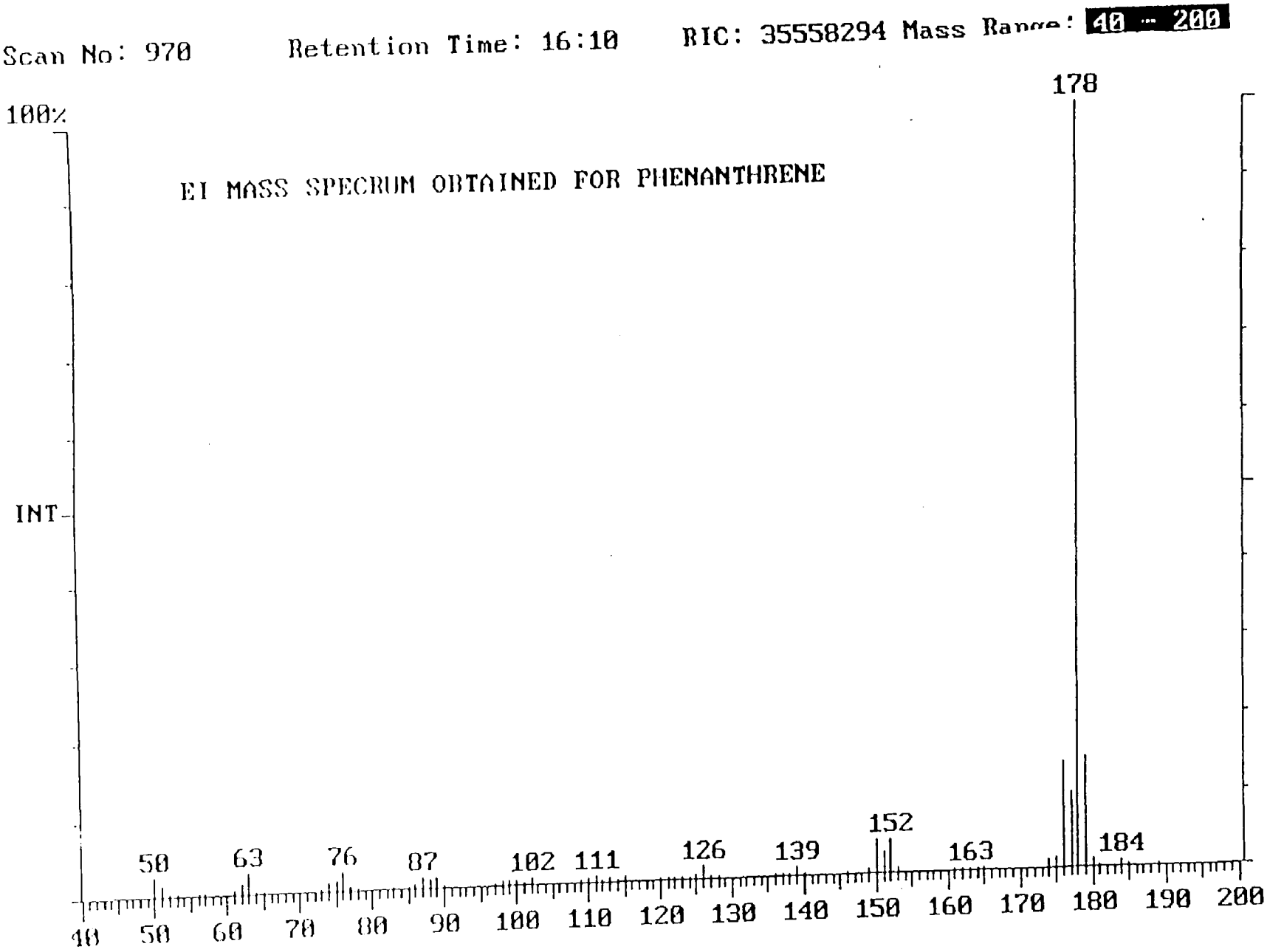
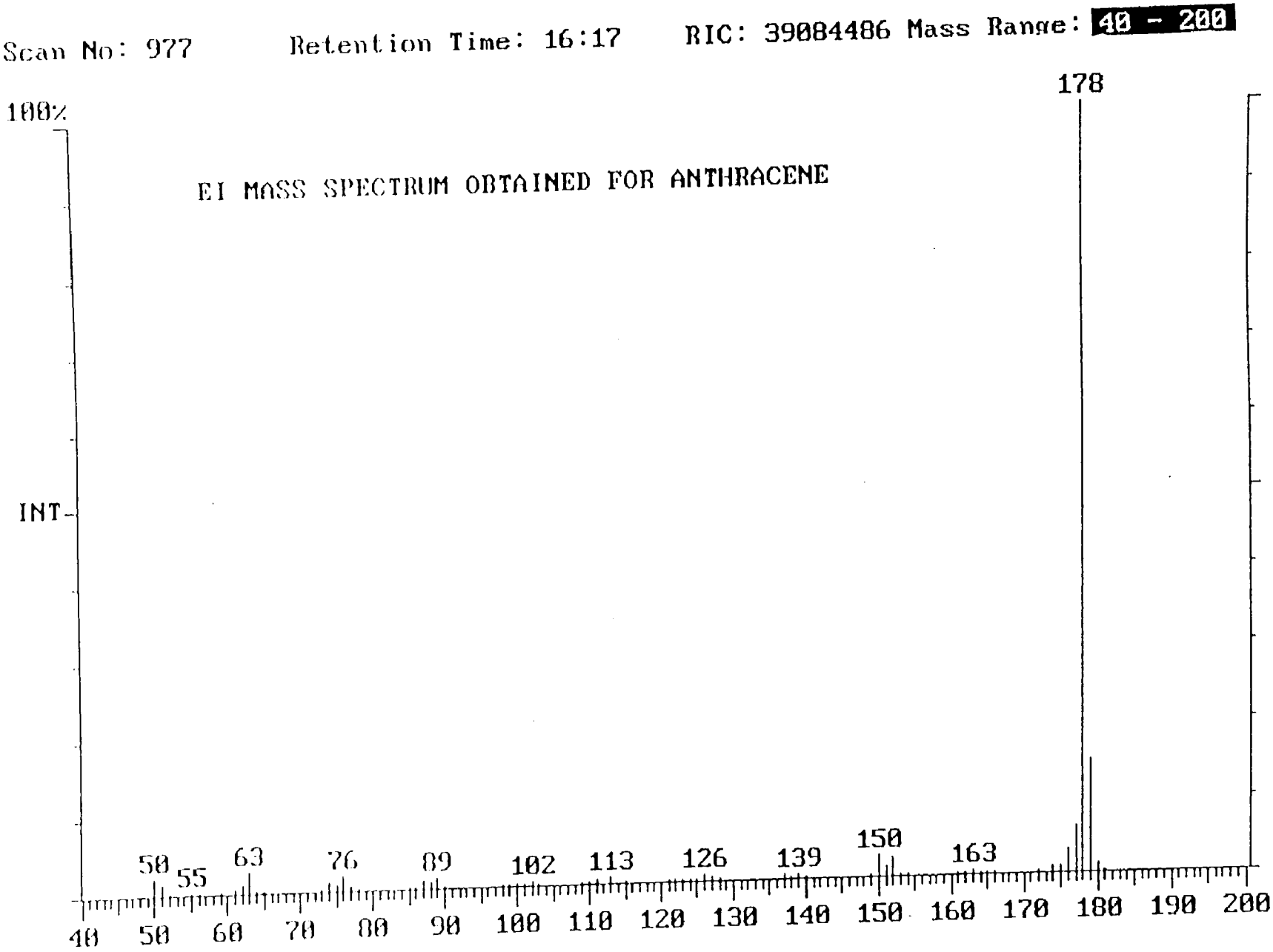
Retention Time: 9:08
RIC: 14301250 Mass Range: 40 - 180
100%
INT
EI MASS SPECTRUM OBTAINED FOR
NAPHTHALENE
128
102
50
63
75
87
55
113
141
148
165
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180


Scan No: 845 Retention Time: 14:05 RIC: 23426814 Mass Range: 40 - 180
Peaks: 78 Base Pk: 166 Ioniz: 27 us Int: 7718518 100.00% = 7718518
100%
EI MASS SPECTRUM OBTAINED FOR FLUORENE
INT
166
139
115
63
50
55
69
74
82
87
98
126
150
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180


Scan No: 970
Retention Time: 16:10
RIC: 35558294 Mass Range: 40 -- 200
100%
EI MASS SPECRUM OBTAINED FOR PHENANTHRENE
INT
178
152
184
50
63
76
87
102
111
126
139
163
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200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RIC: 39084486 Mass Range: 40 - 200
178
100%
EI MASS SPECTRUM OBTAINED FOR ANTHRACENE
INT
150
163
50
55
63
76
89
102
113
126
139
40
50
60
70
80
90
100
110
120
130
140
150
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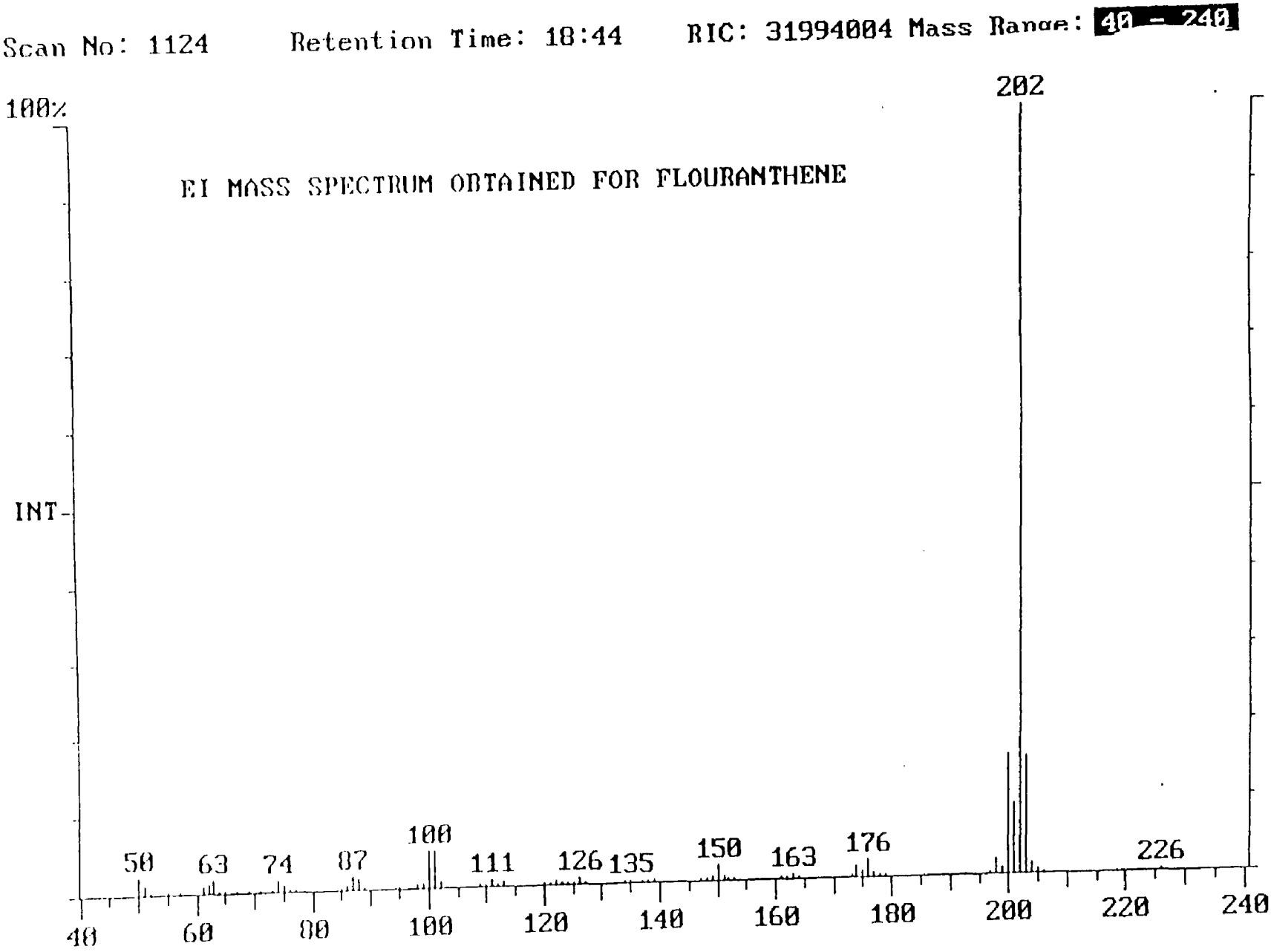
180
190
200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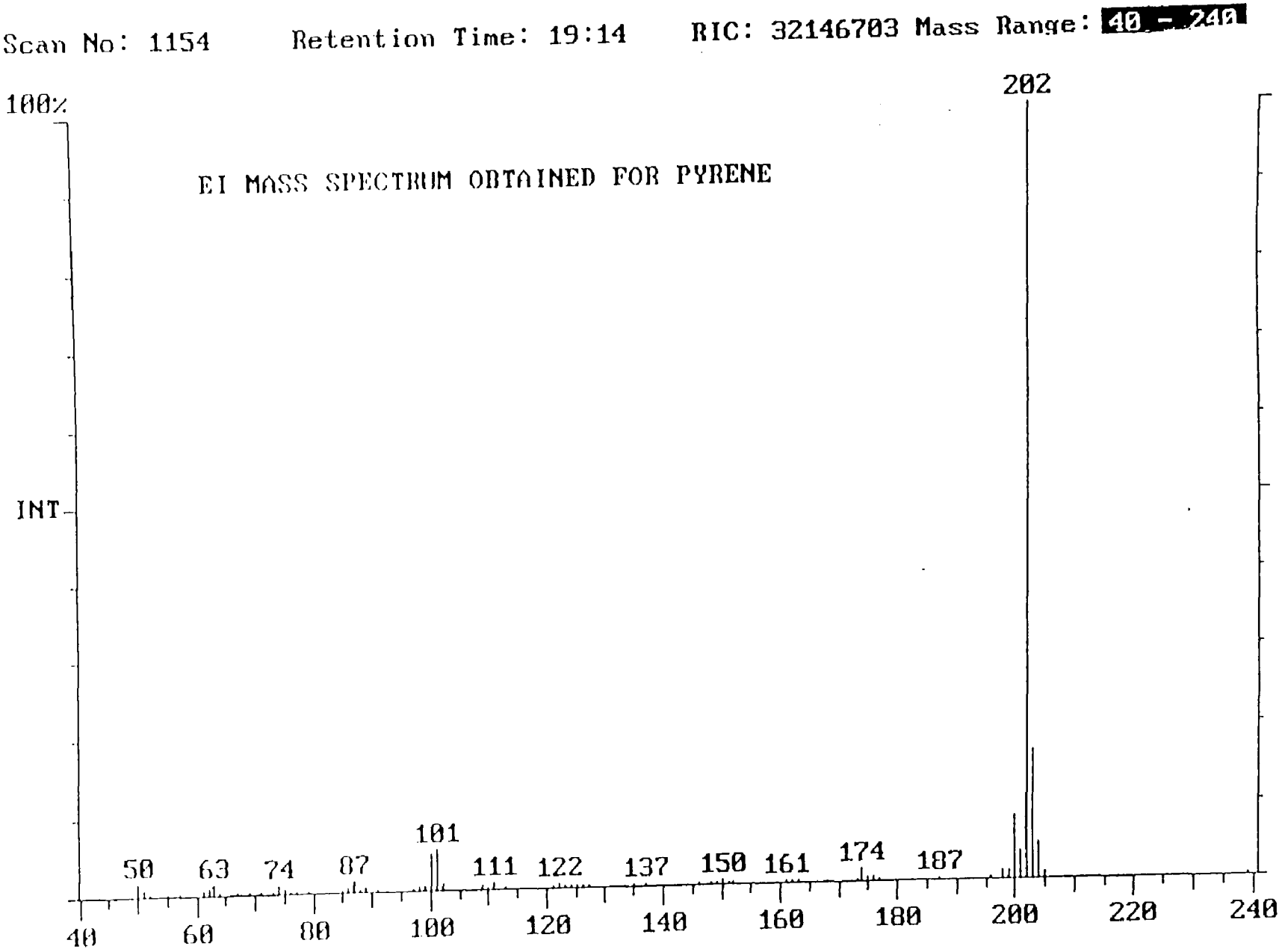
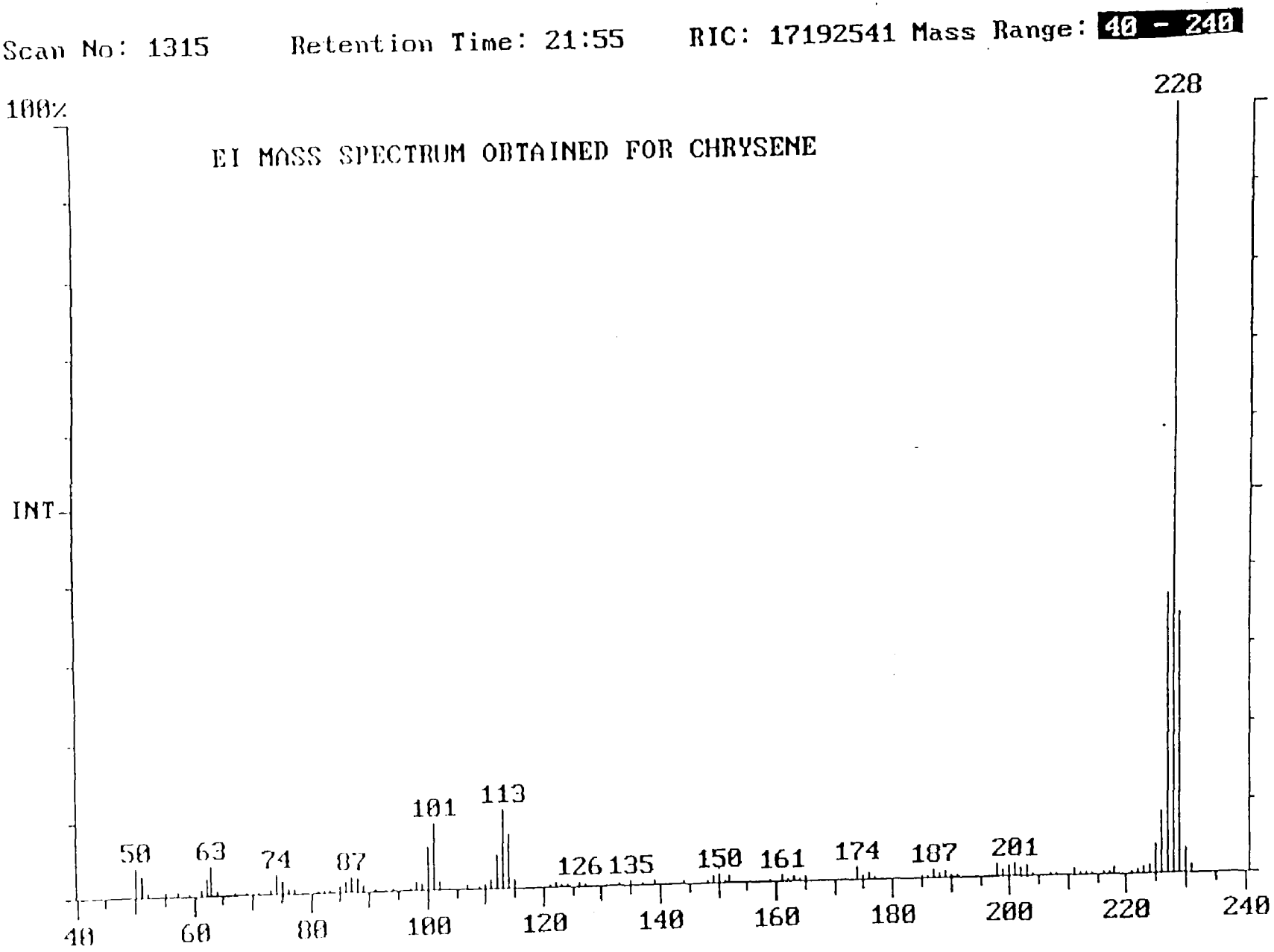
100%
INT
EI MASS SPECTRUM OBTAINED FOR FLOURANTHENE
202
100
50
63
74
87
111
126
135
150
163
176
226
40
60
80
100
120
140
160
180
200
220
240


Scan No: 1154
Retention Time: 19:14
RIC: 32146703 Mass Range: 40 - 240
100%
EI MASS SPECTRUM OBTAINED FOR PYRENE
INT
202
101
50
63
74
87
111
122
137
150
161
174
187
40
60
80
100
120
140
160
180
200
220
240


Scan No: 1315 Retention Time: 21:55 RIC: 17192541 Mass Range: 40 - 240
100%
EI MASS SPECTRUM OBTAINED FOR CHRYSENE
INT
228
50
63
74
87
101
113
126
135
150
161
174
187
201
40
60
80
100
120
140
160
180
200
220
240

TOPLEVEL PARAMETERS

Method Information For: C:\CHEMPC\METHODS\WAFASIM.M

Method Sections To Run:

( ) Save Copy of Method With Data
( ) Pre-Run Cmd/Macro =
(X) Data Acquisition
(X) Data Analysis
( ) Post-Run Cmd/Macro =

Method Comments:
gc/ms of atmospheric residue

END OF TOPLEVEL PARAMETERS

ACQUISITION PARAMETERS

General Information

Inlet : GC
Tune File : ATUNE.U
Acquisition Mode : Sim

Injector Information

Injection Source : Manual

[Purge Information]

Purge A/B	Init. Value	On Time	Off Time
A	On	0.00	0.00
B	Off	0.75	0.00

Temperature Information

[Zone Temperatures]

Det. A : 50 C Off
Det. B : 280 C
Inj. A : 250 C Off
Inj. B : 250 C

[Oven Parameters]

Oven Equib Time : 0.50 min
Oven Max : 325 C
Cryo : Off
Oven : On

[Oven Program]

Initial Temp. : 60 C
Initial Time : 0.00 min

Level	Rate (C/min)	Final Temp. (C)	Final Time (min)
1	10.00	300	5.00
2	0.00		

Next Run Time : 29.00 min

MS Information
-- -----------

Solvent Delay : 5.00 min

EM Absolute : False
EMV Offset : 0.0
Resulting Voltage : 2329.3

[Sim Parameters]

GROUP 1
Group ID : Group 1
Dwell Per Ion : 100 msec.
Low Resolution : No
Group Start Time : 1.00
Ion Plotted : 128.00
Ions In Group :128.00 64.00 166.00 83.00 178.00
89.00 202.00 101.00 228.00 114.00
317.85 245.90

[Real Time Plot Parameters]

Plotting Active : True
Time Window : 20 min
Total Ion Max : 62464
Ion Max : 6248

END OF ACQUISITION PARAMETERS

DATA ANALYSIS PARAMETERS

Method Name: C:\CHEMPC\METHODS\WAFASIM.M

Percent Report Settings

Sort By: Signal

Output Destination
    Screen: Yes
    Printer: Yes
    File: No

Integration Events: AutoIntegrate

Generate Report During Run Method: Yes

Signal Correlation Window: 0.020

Qualitative Report Settings

Peak Location of Unknown: Apex

Library to Search	Minimum Quality
nbs54k	0

Integration Events: AutoIntegrate

Report Type: Detailed

Output Destination
    Screen: No
    Printer: Yes
    File: No

Generate Report During Run Method: Yes

Quantitative Report Settings

Report Type: Summary

Output Destination
    Screen: Yes
    Printer: No
    File: No

Generate Report During Run Method: No

Q. R
Calibration Last Updated: Tue May 18 14:56:08 1993
Internal Standard

Reference Window: 5.00 Percent
Non-Reference Window: 5.00 Percent
Correlation Window: 0.03 minutes
Default Multiplier: 1.00
Default Sample Amount: 0.00

TOPLEVEL PARAMETERS

Method Information For: C:\CHEMPC\METHODS\WAFA.M

Method Sections To Run:

(X) Save Copy of Method With Data
( ) Pre-Run Cmd/Macro =
(X) Data Acquisition
(X) Data Analysis
( ) Post-Run Cmd/Macro =

Method Comments:
hydrocarbon group type seperation of crude oils. Using solid phase extraction method. ref.

END OF TOPLEVEL PARAMETERS

ACQUISITION PARAMETERS

General Information

Inlet : GC
Tune File : ATUNE.U
Acquisition Mode : Scan

Injector Information

Injection Source : Manual

[Purge Information]

Purge A/B	Init. Value	On Time	Off Time
A	On	0.00	0.00
B	Off	0.75	0.00

Temperature Information

[Zone Temperatures]

Det. A : 50 C Off
Det. B : 280 C
Inj. A : 250 C Off
Inj. B : 250 C

Output Destination
    Screen: Yes
    Printer: Yes
    File: No

Integration Events: AutoIntegrate

Generate Report During Run Method: Yes

Signal Correlation Window: 0.020

Qualitative Report Settings

Peak Location of Unknown: Apex

Library to Search	Minimum Quality
nbs54k	0

Integration Events: AutoIntegrate

Report Type: Summary

Output Destination
    Screen: No
    Printer: Yes
    File: No

Generate Report During Run Method: Yes

Quantitative Report Settings

Report Type: Summary

Output Destination
    Screen: No
    Printer: Yes
    File: No

Generate Report During Run Method: Yes

Calibration Last Updated:
Internal Standard

Reference Window: 5.00 Percent
Non-Reference Window: 5.00 Percent
Correlation Window: 0.03 minutes
Default Multiplier: 1.00
Default Sample Amount: 0.00

Compound Information

*** Empty Quantitation Database ***

Method: WAFA.M Thu Aug 11 18:39:54 1994

[Oven Parameters]

Oven Equib Time : 0.50 min
Oven Max : 325 C
Cryo : Off
Oven : On

[Oven Program]

Initial Temp. : 60 C
Initial Time : 0.00 min

Level	Rate (C/min)	Final Temp. (C)	Final Time (min)
1	10.00	300	5.00
2	0.00		

Next Run Time : 29.00 min

MS Information

Solvent Delay : 5.00 min

EM Absolute : False
EMV Offset : 0.0
Resulting Voltage : 2329.3

[Sim Parameters]

GROUP 1
Group ID : Group 1
Dwell Per Ion : 100 msec.
Low Resolution : No
Group Start Time : 1.00
Ion Plotted : 128.00
Ions In Group :128.00 64.00 166.00 83.00 178.00
89.00 202.00 101.00 228.00 114.00
317.85 245.90

[Real Time Plot Parameters]

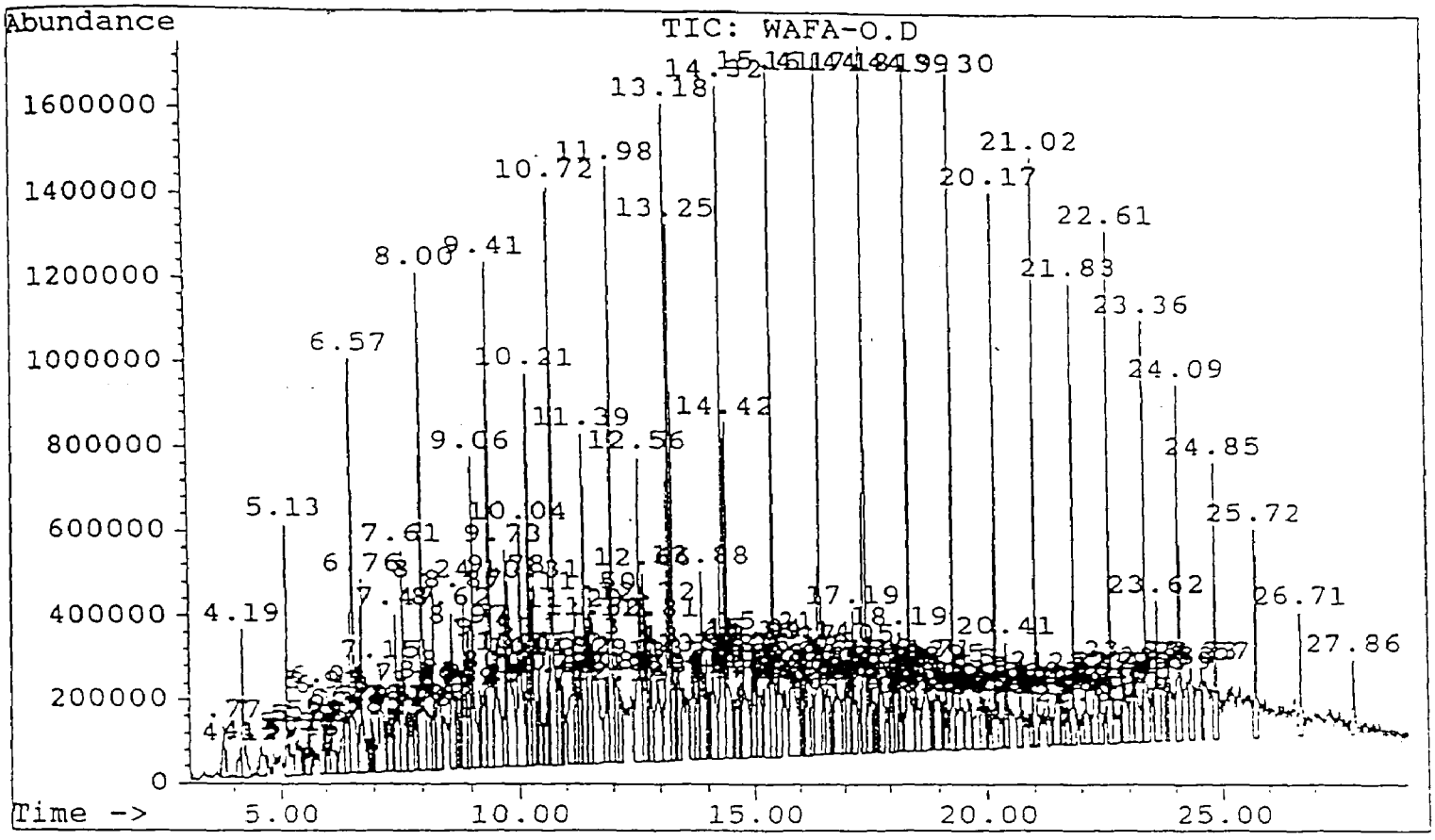
Plotting Active : True
Time Window : 20 min
Total Ion Max : 62464
Ion Max : 6248

END OF ACQUISITION PARAMETERS

DATA ANALYSIS PARAMETERS

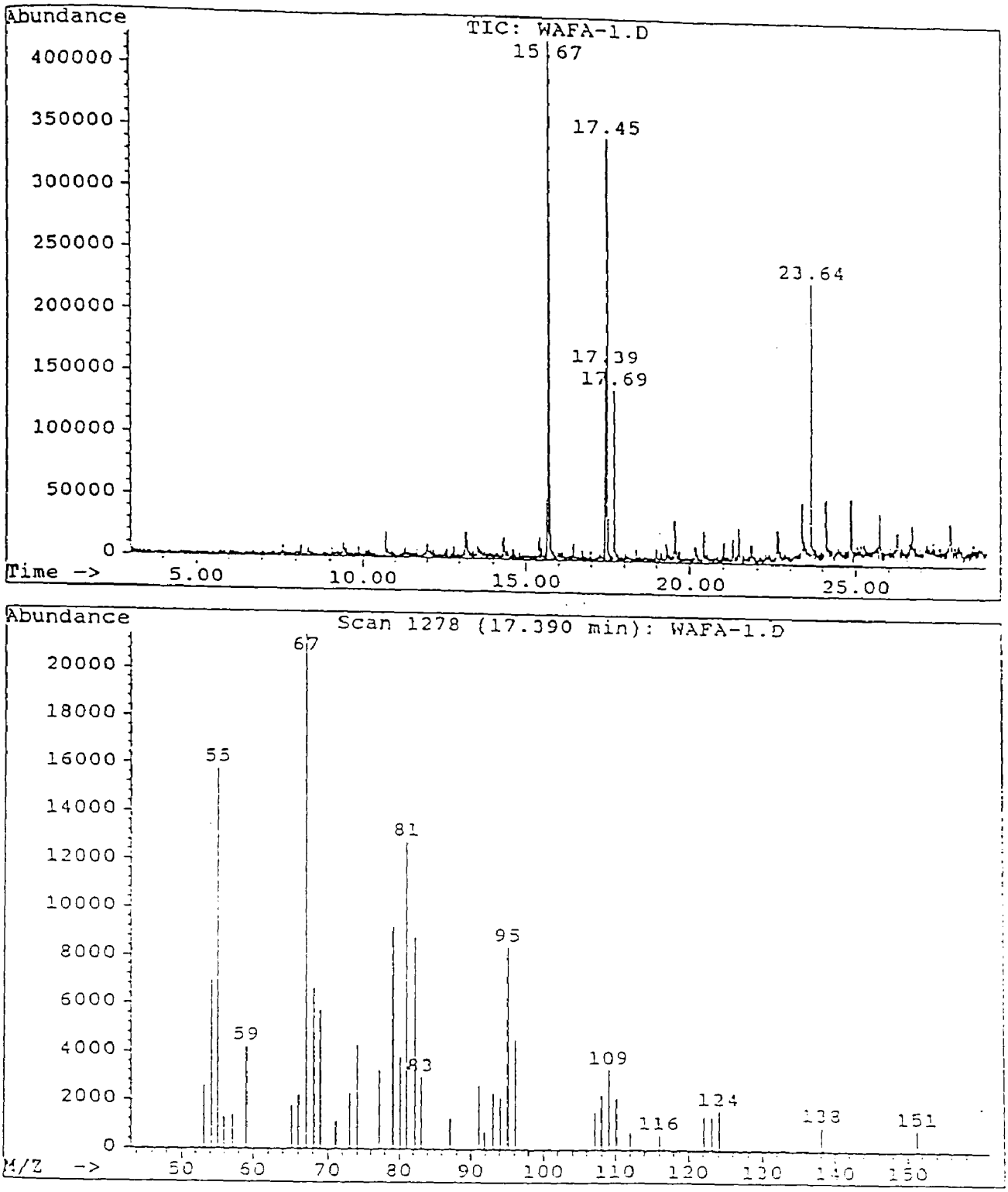
Method Name: C:\CHEMPC\METHODS\WAFASIM.M

File: A:\WAFA-O.D
Operator: WAFA
Date Acquired: 8 Dec 93 4:04 pm
Method File: WAFA.M
Sample Name: FRACTION 1 SFE METHD WITH HEXANE SOLVENT
Misc Info: 1ul injection
ALS vial: 1



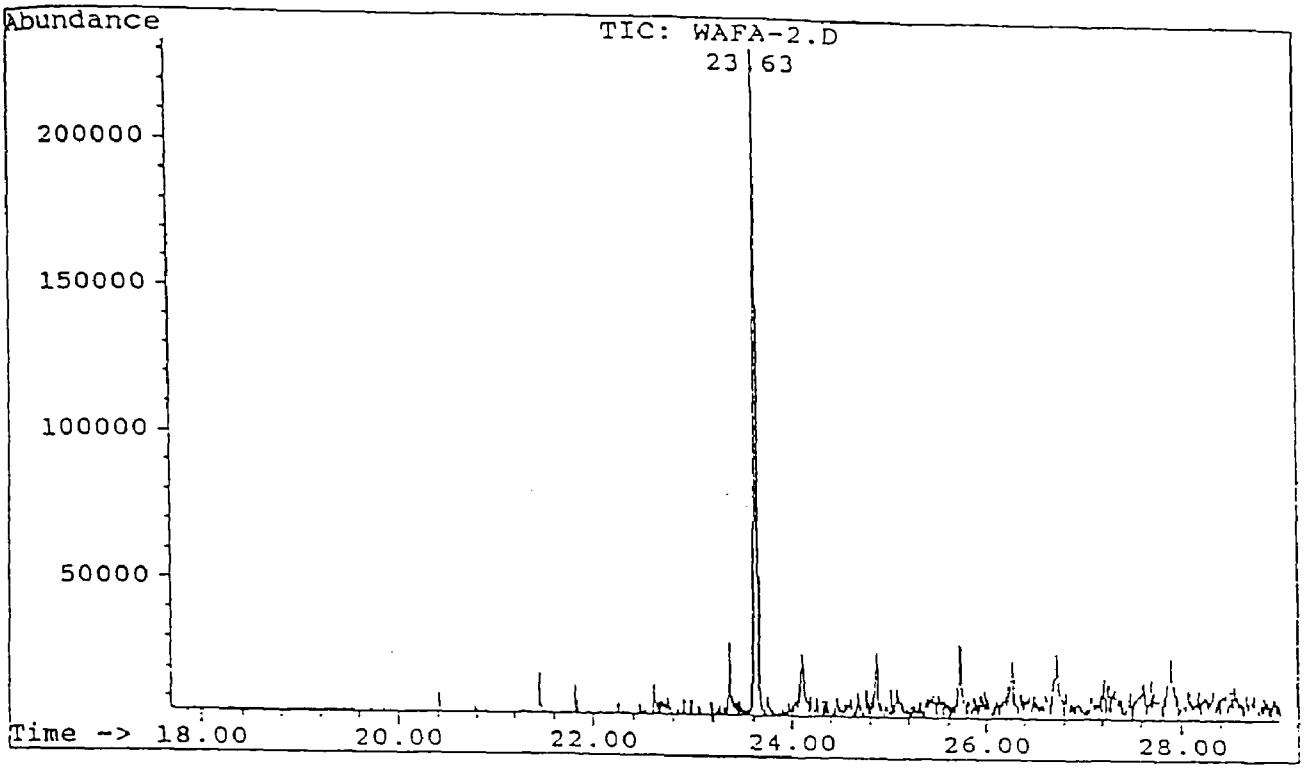
Appendix: 4.1 crude oil sample ; fraction 1 by SFE method with hexane solvent then analysis by GC/MS. Column conditions see chapter 4.

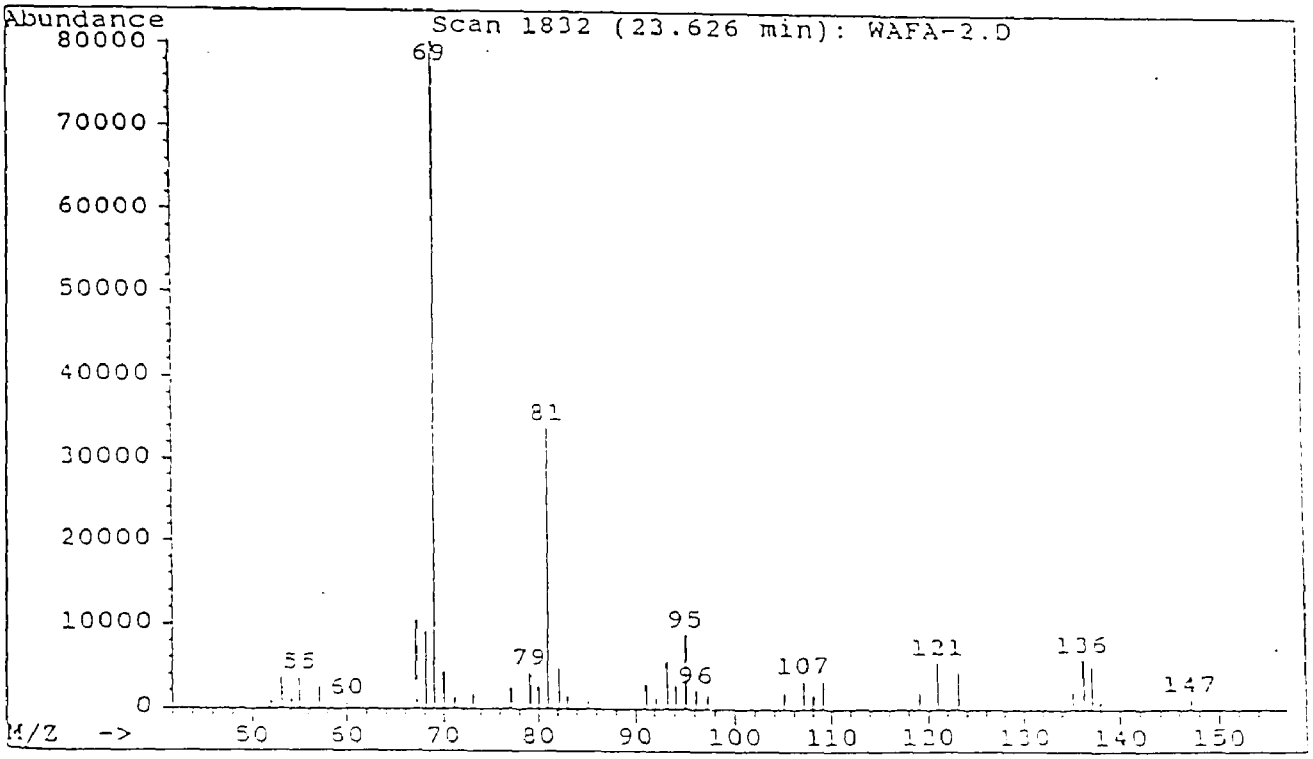
FIle: A:\WAFA-1.D
Operator: WAFA
Date Acquired: 9 Dec 93 12:48 pm
Method File: WAFA.M
Sample Name:
Misc Info: CRUDE OIL FRACTION 2 WITH SFE EXTR "DICHLOM
ALS vial: 1 0.1ul enjection DICHLORMETHANE AS SOLVENT



4.2 Crude oil sample fraction 2 by SFE method with dichloromethane as solvent the analysis by GC/MS. Column conditions same as above.

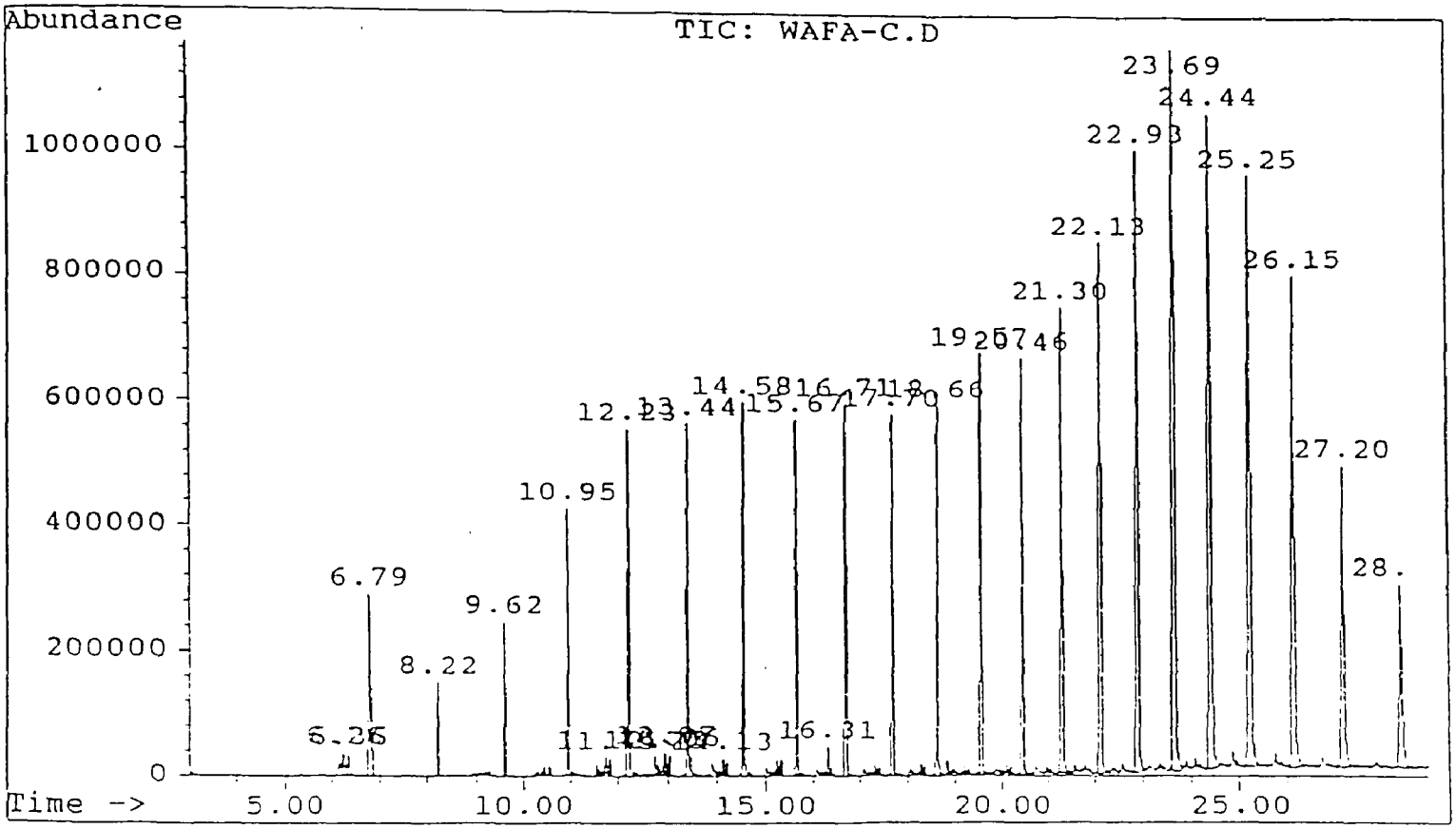
File: A:\WAFA-2.D
Operator: WAFA
Date Acquired: 9 Dec 93 1:27 pm
Method File: WAFA.M
Sample Name:
Misc Info: CRUDE OIL FRACTION3 WITH SFE EXTR "DICHLOM'
ALS vial: 1 0.1ul enjection DICHLORMETHANE AS SOLVENT





4.3 Crude oil sample fraction 3 by SFE method with dichloromethane as solvent then analysis with GC/MS.

File: A:\WAFA-C.D
Operator: WAFA
Date Acquired: 28 Sep 93 6:07 pm
Method File: WAFA.M
Sample Name: SOXHLET EXTRACTION; SAMPLE NO 3
Misc Info: 1 ul INJECTION
ALS vial: 1



Appendix 4.4 Soxhlet extraction of sample 3 from Methanol Plantwith hexane as solvent then analysis by GC/MS. Column conditions see chapter 4.

APPENDIX Chapter 5:

5.1 Classical elemental analysis was reported as being present for sample 1 from Urea plant of Sirte oil Company Libya.

Mr. M. HART
MICRO ANALYTICAL LABORATORY
DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF MANCHESTER
MANCHESTER M13 9PL

Telephone : 061 - 275 4595

APPLICANTS NAME DR J WINTER
ADDRESS UNIVERSITY OF GLAMORGAN

TELEPHONE No.....
ORDER No. 01040
SAMPLE REF NO. SAMPLE 1
ELEMENTS PRESENT.....
ANALYSE FOR C N Al Si

M Pt/B Pt..... SOLVENT.....
TYPE OF COMPOUND OR STRUCTURE (if poss).....

STATE COSHH HAZARD LEVEL (V H M or L) AND LIST KNOWN OR SUSPECTED HAZARDS TO HEALTH AND SAFETY AND GIVE PRECAUTIONS

SENSITIVE TO:- AIR ☐ OXYGEN ☐ LIGHT ☐ MOISTURE ☐

OTHER COMMENTS

PLEASE GIVE APPROX. PERCENTAGES OF ELEMENTS PRESENT IN THE EXPECTED COLUMN.

	EXPECTED	FOUND	CHARGE
C		26.3	
H		5.9	
N		40.8	
Cl			
Br			
I			
S			
F			
P			
Mol.Wt.			
Metal	Al < 10%	0	
Other	Si < 1%	< 30 ppm	

COMMENTS TOTAL CHARGE = £43-00

DATE RECEIVED 20-7-93

DATE REPORTED 22-7-93

SIGNED M. Jennings pp M. Hart

FORM TO BE FORWARDED COMPLETE (ie. IN DUPLICATE) TOGETHER WITH SAMPLE

5.2 Classical elemintal analysis was reported as being present

for sample 2 from Sahel gas field, Sirte oil Company Libya.

Mr. M. HART
MICRO ANALYTICAL LABORATORY
DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF MANCHESTER
MANCHESTER M13 9PL

Telephone : 061 - 275 4595

APPLICANTS NAME DR J WINTER
ADDRESS UNIVERSITY OF GLAMORGAN

TELEPHONE No.
ORDER No. 01040
SAMPLE REF NO. SAMPLE 2
ELEMENTS PRESENT
ANALYSE FOR C N Al Si

M Pt/B Pt SOLVENT
TYPE OF COMPOUND OR STRUCTURE (if poss)

STATE COSHH HAZARD LEVEL (V H M or L) AND LIST KNOWN OR SUSPECTED HAZARDS TO HEALTH AND SAFETY AND GIVE PRECAUTIONS

SENSITIVE TO:- AIR ☐ OXYGEN ☐ LIGHT ☐ MOISTURE ☐
OTHER COMMENTS

PLEASE GIVE APPROX. PERCENTAGES OF ELEMENTS PRESENT IN THE EXPECTED COLUMN.

	EXPECTED	FOUND	CHARGE
C		4.8	
H		3.4	
N		0	
Cl			
Br			
I			
S			
F.			
P			
Metals.	Rpt Al	6.9	
Metal	Al < 10%	7.1	
Other	Si 1-5%	0.4	

COMMENTS TOTAL CHARGE · 1:43-C

Carbonate present.

DATE RECEIVED 20-7-93
DATE REPORTED 23-7-93

SIGNED M. Jennings pp M. HART

FORM TO BE FORWARDED COMPLETE (ie. IN DUPLICATE) TOGETHER WITH SAMPLE

5.3 Classical elemintal analysis was reported as bieng present

for sample 3 from Methanol plant, Sirte oil Company Libya.

Mr. M. HART
MICRO ANALYTICAL LABORATORY
DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF MANCHESTER
MANCHESTER M13 9PL

Telephone : 061 - 275 4595

APPLICANTS NAME DR J WINTER
ADDRESS UNIVERSITY OF GLAMORGAN

TELEPHONE No.
ORDER No. 01040
SAMPLE REF NO. SAMPLE 3
ELEMENTS PRESENT
ANALYSE FOR C N Al Si

M Pt/B Pt. SOLVENT
TYPE OF COMPOUND OR STRUCTURE (if poss)

STATE COSHH HAZARD LEVEL (V H M or L) AND
LIST KNOWN OR SUSPECTED HAZARDS TO HEALTH
AND SAFETY AND GIVE PRECAUTIONS

SENSITIVE TO:- AIR ☐ OXYGEN ☐ LIGHT ☐ MOISTURE ☐
OTHER COMMENTS

PLEASE GIVE APPROX. PERCENTAGES OF ELEMENTS
PRESENT IN THE EXPECTED COLUMN.

	EXPECTED	FOUND	CHARGE
C		85.0	
H		15.0	
N		0	
Cl			
Br			
I			
S			
Fe		2.4 ppm	F.O.C
P			
Mol.Wt.			
Metal	Al ?	0	
Other	Si ?	< 1 ppm	

COMMENTS TOTAL CHARGE = 143-cc

DATE RECEIVED 20-7-93
DATE REPORTED 23-7-93

SIGNED

FORM TO BE FORWARDED COMPLETE (ie. IN DUPLICATE) TOGETHER WITH SAMPLE M. Jennings pp M. HART